


NATIONAL SCIENCE CURRICULUM MATERIALS

Rates of Chemical Reactions

R. J. STANLEY





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NATIONAL SCIENCE CURRICULUM MATERIALS



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Rates of Chemical Reactions

R. J. Stanley

St Peter's College, Adelaide

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PERIODIC TABLE

³ Li 6.94	⁴ Be 9.01	² He 4.00
¹¹ Na 23.0	¹² Mg 24.3	¹⁰ Ne 20.2
¹⁹ K 39.1	²⁰ Ca 40.1	¹⁸ Ar 39.9
³⁷ Rb 85.5	³⁸ Sr 87.6	³⁶ Kr 83.8
⁵⁵ Cs 132.9	⁵⁶ Ba 137.3	⁵⁴ Xe 131.3
⁸⁷ Fr (223)	⁸⁸ Ra (226)	⁸⁶ Rn (222)

²¹ Sc 45.0	²² Ti 47.9	²³ V 50.9	²⁴ Cr 52.0	²⁵ Mn 54.9	²⁶ Fe 55.8	²⁷ Co 58.9	²⁸ Ni 58.7	²⁹ Cu 63.5	³⁰ Zn 65.4
³⁹ Y 88.9	⁴⁰ Zr 91.2	⁴¹ Nb 92.9	⁴² Mo 95.9	⁴³ Tc (99)	⁴⁴ Ru 101.1	⁴⁵ Rh 102.9	⁴⁶ Pd 106.4	⁴⁷ Ag 107.9	⁴⁸ Cd 112.4
⁵⁷⁻⁷¹ La-Lu	⁷² Hf 178.5	⁷³ Ta 180.9	⁷⁴ W 183.9	⁷⁵ Re 186.2	⁷⁶ Os 190.2	⁷⁷ Ir 192.2	⁷⁸ Pt 195.1	⁷⁹ Au 197.0	⁸⁰ Hg 200.6
⁸⁹⁻¹⁰³ Ac-Lw	¹⁰⁴	¹⁰⁵							

⁵ B 10.8	⁶ C 12.01	⁷ N 14.01	⁸ O 16.00	⁹ F 19.0	¹⁰ Ne 20.2
¹³ Al 27.0	¹⁴ Si 28.1	¹⁵ P 31.0	¹⁶ S 32.1	¹⁷ Cl 35.5	¹⁸ Ar 39.9
³¹ Ga 69.7	³² Ge 72.6	³³ As 74.9	³⁴ Se 79.0	³⁵ Br 79.9	³⁶ Kr 83.8
⁴⁹ In 114.8	⁵⁰ Sn 118.7	⁵¹ Sb 121.8	⁵² Te 127.6	⁵³ I 126.9	⁵⁴ Xe 131.3
⁸¹ Tl 204.4	⁸² Pb 207.2	⁸³ Bi 209.0	⁸⁴ Po (210)	⁸⁵ At (210)	⁸⁶ Rn (222)

⁵⁷ La 138.9	⁵⁸ Ce 140.1	⁵⁹ Pr 140.9	⁶⁰ Nd 144.2	⁶¹ Pm (145)	⁶² Sm 150.4	⁶³ Eu 152.0	⁶⁴ Gd 157.2	⁶⁵ Tb 158.9	⁶⁶ Dy 162.5	⁶⁷ Ho 164.9	⁶⁸ Er 167.3	⁶⁹ Tm 168.9	⁷⁰ Yb 173.0	⁷¹ Lu 175.0
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⁸⁹ Ac (227)	⁹⁰ Th 232.0	⁹¹ Pa (231)	⁹² U 238.0	⁹³ Np (237)	⁹⁴ Pu (242)	⁹⁵ Am (243)	⁹⁶ Cm (248)	⁹⁷ Bk (247)	⁹⁸ Cf (249)	⁹⁹ Es (254)	¹⁰⁰ Fm (253)	¹⁰¹ Md (256)	¹⁰² No (254)	¹⁰³ Lw (257)
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Parentetical values are mass numbers of the isotopes with longest half-lives

INTERNATIONAL ATOMIC WEIGHTS

(Atomic Weights relative to $^{12}\text{C} = 12$ exactly)

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
1	Hydrogen	H	1.008	31	Gallium	Ga	69.72
2	Helium	He	4.003	32	Germanium	Ge	72.59
3	Lithium	Li	6.939	33	Arsenic	As	74.92
4	Beryllium	Be	9.012	34	Selenium	Se	78.96
5	Boron	B	10.81	35	Bromine	Br	79.91
6	Carbon	C	12.01	36	Krypton	Kr	83.80
7	Nitrogen	N	14.01	37	Rubidium	Rb	85.47
8	Oxygen	O	16.00	38	Strontium	Sr	87.62
9	Fluorine	F	19.00	39	Yttrium	Y	88.91
10	Neon	Ne	20.18	40	Zirconium	Zr	91.22
11	Sodium	Na	22.99	41	Niobium	Nb	92.91
12	Magnesium	Mg	24.31	42	Molybdenum	Mo	95.94
13	Aluminium	Al	26.98	43	Technetium*	Tc	(99)
14	Silicon	Si	28.09	44	Ruthenium	Ru	101.1
15	Phosphorus	P	30.97	45	Rhodium	Rh	102.9
16	Sulphur	S	32.06	46	Palladium	Pd	106.4
17	Chlorine	Cl	35.45	47	Silver	Ag	107.9
18	Argon	Ar	39.95	48	Cadmium	Cd	112.4
19	Potassium	K	39.10	49	Indium	In	114.8
20	Calcium	Ca	40.08	50	Tin	Sn	118.7
21	Scandium	Sc	44.96	51	Antimony	Sb	121.8
22	Titanium	Ti	47.90	52	Tellurium	Te	127.6
23	Vanadium	V	50.94	53	Iodine	I	126.9
24	Chromium	Cr	52.00	54	Xenon	Xe	131.3
25	Manganese	Mn	54.94	55	Caesium	Cs	132.9
26	Iron	Fe	55.85	56	Barium	Ba	137.3
27	Cobalt	Co	58.93	57	Lanthanum	La	138.9
28	Nickel	Ni	58.71	58	Cerium	Ce	140.1
29	Copper	Cu	63.54	59	Praseodymium	Pr	140.9
30	Zinc	Zn	65.37	60	Neodymium	Nd	144.2

*Unstable elements

Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

INTERNATIONAL ATOMIC WEIGHTS

(Atomic Weights relative to $^{12}\text{C} = 12$ exactly)

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
61	Promethium*	Pm	(145)	86	Radon*	Rn	(222)
62	Samarium	Sm	150.4	87	Francium*	Fr	(223)
63	Europium	Eu	152.0	88	Radium*	Ra	(226)
64	Gadolinium	Gd	157.3	89	Actinium*	Ac	(227)
65	Terbium	Tb	158.9	90	Thorium*	Th	232.0
66	Dysprosium	Dy	162.5	91	Protactinium*	Pa	(231)
67	Holmium	Ho	164.9	92	Uranium*	U	238.0
68	Erbium	Er	167.3	93	Neptunium*	Np	(237)
69	Thulium	Tm	168.9	94	Plutonium*	Pu	(242)
70	Ytterbium	Yb	173.0	95	Americium*	Am	(243)
71	Lutetium	Lu	175.0	96	Curium*	Cm	(248)
72	Hafnium	Hf	178.5	97	Berkelium*	Bk	(247)
73	Tantalum	Ta	180.9	98	Californium*	Cf	(249)
74	Tungsten	W	183.9	99	Einsteinium*	Es	(254)
75	Rhenium	Re	186.2	100	Fermium*	Fm	(253)
76	Osmium	Os	190.2	101	Mendelevium*	Md	(256)
77	Iridium	Ir	192.2	102	Nobelium*	No	(254)
78	Platinum	Pt	195.1	103	Lawrencium*	Lw	(257)
79	Gold	Au	197.0	104	(Kurchatovium)		
80	Mercury	Hg	200.6				
81	Thallium	Tl	204.4				
82	Lead	Pb	207.2				
83	Bismuth	Bi	209.0				
84	Polonium*	Po	(210)				
85	Astatine*	At	(210)				

*Unstable elements

Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

After the completion of this unit, you should know about:

- the wide range in rate for different chemical reactions;
- the wide range in rate for the same chemical reactions when conditions are changed;
- defining and measuring reaction rate;
- the inconsistency of rate and its dependence on the factors:
 - (a) concentration,
 - (b) temperature,
 - (c) catalysts and catalysis;
- the measurement of concentration changes;
- the collision theory as a theoretical background to reaction rates; and
- reaction mechanism involving the formation of activated complexes.

You should be able to:

- solve simple rate problems;
- construct graphs and interpret data in order to calculate specific rate; and
- measure a reaction rate in the laboratory.

Introduction

Why should a car increase speed when the accelerator is depressed? Those with some knowledge of motor mechanics will answer that depressing the accelerator allows more petrol and air to vaporize through the carburettor into the combustion chamber of the engine. But why should more petrol and air increase engine revolutions, so increasing the speed of the vehicle? It might come as a surprise that the chemist, rather than the mechanic, can best supply the answer.

This problem is one of many studied and answered under the general topic of 'rates of chemical reactions'.

Most of you are aware that different chemical reactions occur at different rates, but you may be unaware of how great these differences are. Some reactions are slow, for example, the rusting of iron; some are moderate, for example, the burning of a wood fire on a cold winter's evening; some are uncomfortably fast, for example, that Australian summer hazard, the bushfire; and some are instantaneous, for example, an explosion.

Not only do different reactions occur at different rates, but the same reaction can also have an enormous range in reaction rates, depending on conditions. For example, the reaction between the gases hydrogen and oxygen at room temperature is so slow that, if the whole world's atmosphere was made up of hydrogen and oxygen in a volume ratio of two to one, only a few molecules would react in a century. However, if you lit a match, that is increased the temperature of some reactants, the result might well be described as 'world shattering'. An increase in temperature has a spectacular effect on the rate for this reaction and for many others. Why?

The study of reaction rates will help you answer these questions. Because it also provides an insight into the way in which reactants come together and rearrange themselves to form products, it will help you develop a more thorough understanding of chemistry.

The practical application of reaction rate theory is also important. The chemist in industry often meets a reaction which is both desirable and economically feasible, but goes either too fast or too slow. It is his knowledge of reaction rates that enables such a reaction to be brought to the desired rate for effective com-

mercial development and, it is to be hoped, for the eventual betterment of mankind.

The Concept of Rate of Chemical Reaction

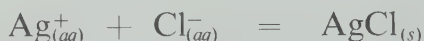
The Meaning of Reaction Rate

In the introduction, the term 'reaction rate' was used without definition. It is now necessary to determine what is meant exactly by 'reaction rate' or 'rate of reaction'. The term reaction, itself, implies that a chemical reaction has occurred. That is, the reactants are, to some extent, changed into products. Rate implies time. Hence reaction rate means a chemical reaction in which time is considered. Observations in the laboratory have shown that chemical reactions, considered from a time point of view, can be conveniently grouped under three arbitrarily chosen headings.

These are:

(a) Reactions fast enough to be regarded as instantaneous

An example here is the reaction between silver ions, Ag^+ and chloride ions, Cl^- , brought about by mixing solutions of these two ions. The precipitation of white silver chloride is instantaneous:



(b) Slow enough to be observable

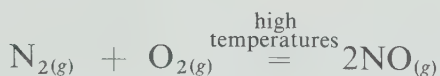
An example of a slower reaction is that which occurs when a coil of magnesium ribbon is dropped into a solution of dilute acid. The evolution of hydrogen is observable, and the reaction takes an observable time for completion.



(c) Apparently no reaction at room temperature, but the reaction may proceed at higher temperatures

The reaction between nitrogen, N_2 , and oxygen, O_2 , is an example.

There appears to be no reaction at all at room temperature but at high temperatures some formation of nitric oxide is possible.



During an electrical storm, lightning produces such a synthesis from the oxygen and nitrogen in the air.

But how fast is fast, and how slow is slow? Obviously, the time factor must be measured, as different people would give different answers to this question.

It is simpler to begin a time study with reactions classified under (b), (that is, reactions with observable rates), so that complications involving very small or very large intervals of time are not introduced. It is difficult to study the rate of a reaction taking 10^{-6} seconds to occur!

Consider the example given in (b) above. When magnesium is added to dilute hydrochloric acid, hydrogen is evolved and the magnesium gradually disappears. As magnesium is used hydrogen is formed. One method for determining the rate for this reaction would be to weigh the magnesium to be used and, after a certain interval of time, remove the unused magnesium and reweigh it. The amount of magnesium used over an interval of time would be a measure of the rate.

Alternatively (and this is easier experimentally) weigh the magnesium, and then determine the time taken for this sample to react completely.

The rate for this reaction could then be expressed as the variation in concentration of a reactant, namely magnesium, with time, just as the speed of a vehicle is measured as distance travelled in a certain time—expressed as miles per hour.

Is another alternative possible? Yes, if a device for the collection of the hydrogen evolved could be attached. Then the amount of evolved hydrogen can be measured, and the rate could be expressed as the variation in concentration of a product, namely hydrogen, with time.

For the example discussed, the rate could be quantitatively expressed as either

$$\text{reaction rate} = \frac{\text{amount of magnesium reacted}}{\text{time (in seconds) for reaction}}$$

$$\text{or reaction rate} = \frac{\text{amount of hydrogen evolved}}{\text{time (in seconds) for reaction}}$$

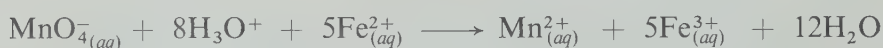
The balanced equation for this reaction:



shows that for every mole of magnesium consumed there is one mole of hydrogen evolved. Thus hydrogen is evolved as fast as the magnesium is consumed, which means that the rate in terms of magnesium is numerically the same as the rate in terms of hydrogen.

However, it is important to realize that the rate of production of a product is not necessarily equal to the rate of consumption of a reactant. What this relationship is, will be determined by the **stoichiometry** of the reaction. Stoichiometry comes from the Greek *stoicheion* meaning element, so a literal meaning for this word would be 'measuring elements'. But in chemistry its meaning is much fuller than this: the study of quantitative relationships between reactants and products, as implied by the chemical equation describing the reaction.

Consider the oxidation of the iron II ion, $\text{Fe}_{(aq)}^{2+}$, by acidified permanganate ion, $\text{MnO}_{4(aq)}^-$. The reaction rate expressed in terms of products or in terms of reactants for this reaction:



may or may not be the same. The rate of formation of Mn^{2+} will be the same as that for the removal of MnO_4^- , because the equation shows that for every ion of MnO_4^- reacting there is one ion of Mn^{2+} formed. But both these rates will differ by a factor of five compared with the rates expressed in terms of Fe^{2+} or Fe^{3+} because for every ion of MnO_4^- used there would be five Fe^{2+} ions used and five Fe^{3+} ions formed.

To differentiate between the formation of a product and the consumption of a reactant, positive (+) and negative (−) signs could be used. A positive rate would be one measuring a product's formation, whilst a negative rate would be one measuring a reactant's consumption. However, the use of signs is not necessary as it is the usual practice for the particular participant in the reaction being studied to be specified in any quantitative expression of rate.

The rate of a chemical reaction is an expression giving the variation in the concentration of a participant per unit time.

For an example reaction given by the hypothetical equation:



the rate can be equally as well expressed as

$$\begin{aligned} & \text{(a)} \quad \frac{\text{change in concentration of A}}{\text{time interval}} \\ \text{or (b)} \quad & \frac{\text{change in concentration of B}}{\text{time interval}} \\ \text{or (c)} \quad & \frac{\text{change in concentration of C}}{\text{time interval}} \end{aligned}$$

The concentration units commonly used in reaction rate studies are:

- (a) For reactions in solution, moles per litre (mol l^{-1}).
- (b) For gaseous reactions, (i) moles per litre (mol l^{-1}) or, less frequently, (ii) partial pressures.
- (c) For solids reacting, moles, (mol).

Molar concentrations are represented by square brackets, []. Thus the concentration of reactant A in moles per litre is denoted by [A]. Changes are denoted by Δ ; so a change in concentration of A can be represented as $\Delta[A]$.

Using this symbolism, and R to denote rate, the rates for the hypothetical reaction, $A + 2B \longrightarrow 3C$, may be expressed as:

$$\text{(a)} \quad R_{(A)} = \frac{\Delta[A]}{t}$$

$$\text{(b)} \quad R_{(B)} = \frac{\Delta[B]}{t}$$

if reactants are used, or by:

$$R_{(C)} = \frac{\Delta[C]}{t}$$

if products are used.

PROBLEM

Are $R_{(A)}$, $R_{(B)}$ and $R_{(C)}$, for the above reaction, equal?
If not, how are they related?

Solution

The equation for the reaction $A + 2 B \longrightarrow 3 C$ shows that for each mole of A, 2 moles of B react to form 3 moles of C.

Rates are not equal because, if 1 mole of A is consumed in a given interval of time, 3 moles of C are produced during the same time. Thus the rates are related:

$$\begin{aligned} R_{(A)} &= \frac{1}{2} R_{(B)} = \frac{1}{3} R_{(C)} \\ 3R_{(A)} &= \frac{3}{2} R_{(B)} = R_{(C)} \end{aligned}$$

Do not become confused. Generally only one rate is used for any given reaction and the one chosen will depend on which change in concentration is the easiest to measure accurately under experimental conditions.

For example, in determining the rate for a reaction between $Mg_{(s)}$ and H_3O^+ , the change in concentration of $Mg_{(s)}$ is the easier to determine and hence, the reaction rate would be expressed initially in moles of magnesium per time interval. Having determined the rate in terms of one participant, the rate in terms of any other participant can be calculated from the balanced equation describing the reaction.

Reaction rate has units. If the reaction is in solution, then the units for R would be $\text{mol l}^{-1} \text{s}^{-1}$ if seconds are the time units. Time can be in whatever unit is most suitable, milliseconds for faster reactions, hours for slower reactions.

PROBLEM

0.144g of magnesium ribbon was placed in dilute hydrochloric acid and it took 30 seconds to react completely. What would be the rate for this reaction? ($Mg = 24$)

Solution

$$\text{rate} = \frac{\text{moles of magnesium reacted}}{\text{time interval}}$$

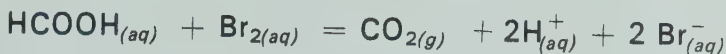
$$0.144\text{g of Mg} = \frac{0.144}{24} \text{ moles of Mg}$$

$$\begin{aligned} \therefore \text{rate} &= \frac{0.144}{24} \times \frac{1}{30} \text{ mol s}^{-1} \\ &= 0.0002 \text{ mol s}^{-1} \end{aligned}$$

$$\therefore \text{rate in terms of magnesium consumed} = 2 \times 10^{-4} \text{ mol s}^{-1}$$

PROBLEM

Bromine will oxidize formic acid to CO_2 ; the balanced equation for this reaction in an aqueous solution is:



If the initial concentration of $\text{Br}_{2(aq)}$ is $1 \times 10^{-2} \text{ M}$ and after 50 seconds the concentration falls to $1 \times 10^{-3} \text{ M}$, determine the rate of reaction in terms of consumption of bromine. What is the rate in terms of (i) $\text{CO}_{2(g)}$ produced, and (ii) $\text{H}^+_{(aq)}$ produced?

Solution

$$\begin{aligned}\text{Rate} &= \frac{\text{moles of bromine reacted}}{\text{time interval}} \\ &= \frac{0.01 - 0.001}{50} \text{ mol l}^{-1} \text{ s}^{-1} \\ &= \frac{0.009}{50} \text{ mol l}^{-1} \text{ s}^{-1} \\ &= 1.8 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}\end{aligned}$$

(i) The equation shows that for every mole of Br_2 reacted, one mole of CO_2 is evolved.

$$\begin{aligned}\therefore \text{rate in terms of } \text{CO}_2 \text{ produced} &= \text{rate in terms of } \text{Br}_2 \text{ reacted} \\ &= 1.8 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}\end{aligned}$$

(ii) For every mole of Br_2 reacted, 2 moles of $\text{H}^+_{(aq)}$ are produced.

$$\therefore \text{rate in terms of } \text{H}^+_{(aq)} \text{ is twice that in terms of } \text{Br}_2, \text{ and } = 3.6 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$$

Is Reaction Rate Constant ?

Any keen observer of the magnesium with dilute acid reaction (*acid-metal reaction*) will report that the reaction is more vigorous at the start than at the finish; a similar report can be made from observations of an *acid-carbonate reaction*. The course of these reactions can be followed by determining the weight changes as the gas is evolved. A simple way to do this is to place a conical flask containing the dilute acid on an open-top pan type of direct reading balance and to add pieces of marble or metal. A loose plug of cotton wool is inserted to prevent acid spray damage and the weight readings are taken at one minute intervals.

Figure 2 shows some typical results summarized in graph form.

What can be learnt from this graph? Consider the first minute of reaction. During this time interval the weight of carbon dioxide or hydrogen evolved is indicated by OX. XY indicates the weight loss from the second one minute time interval and YZ the loss

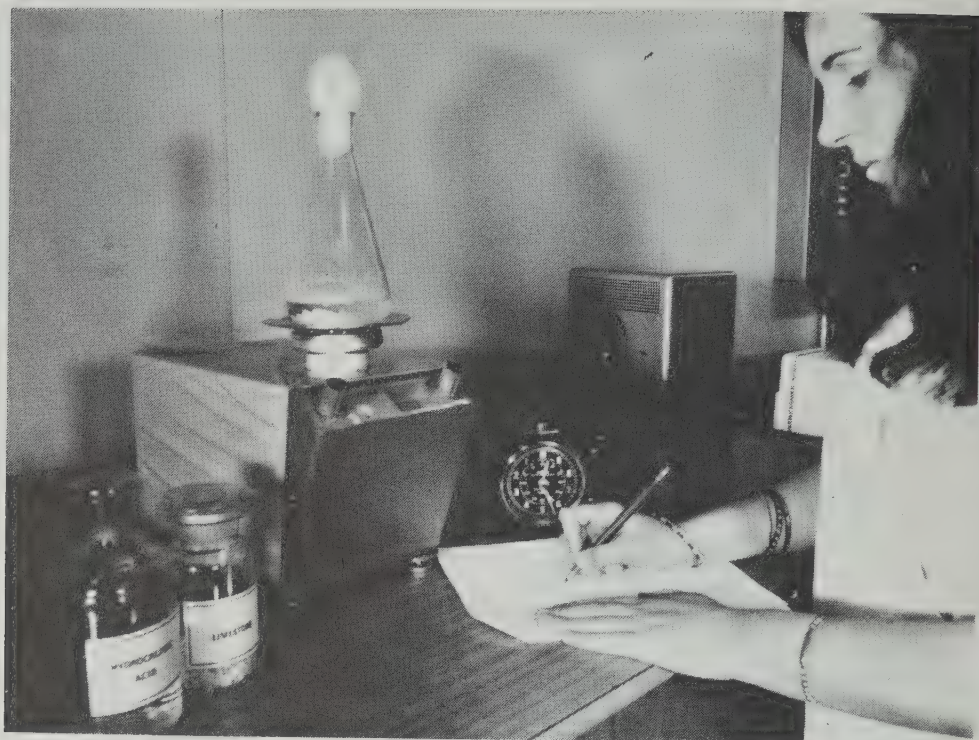


Figure 1. Measuring a reaction rate—here the rate of the reaction between marble (calcium carbonate) and dilute acid is being measured

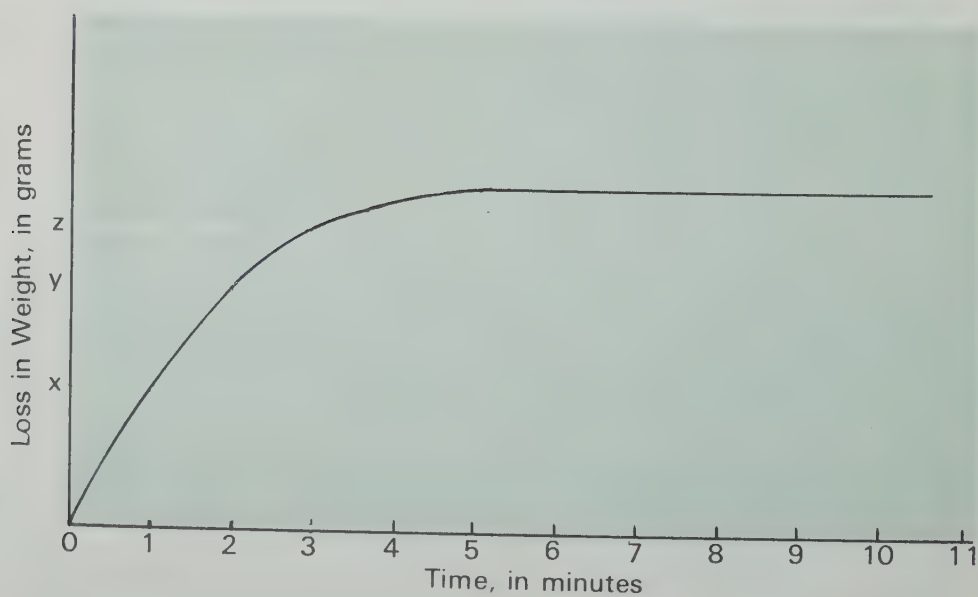


Figure 2

from the third time interval. OX is greater than XY, and XY is greater than YZ. Simply stated, this means that the amount of gas

given off as time increases is becoming smaller and smaller, or the rate of reaction decreases as time increases.

The flat section of the graph shows that no further reaction is occurring. If some marble or metal is left at this stage, then the reaction has stopped because there is no more acid. As the acid is used, so the reaction slows down. *The concentration of acid directly influences the rate of these reactions.*

These and other experiments have shown that for most reactions the rate does in fact change with time; reactions generally become slower as time extends because reactant concentrations decrease. This is just another way of saying that the concentrations of reactants and products show most change at the beginning of a reaction.

Therefore, the answer to the question 'Is reaction rate constant?' is 'No!'. Because rate is not constant, the rate determined in the problems on pages 6 and 7 should be qualified by using the term '**average rate**'. Rates determined over a period of time are *average rates*, because the rate has changed during the time interval.

The rate at a specified time is termed the **specific rate**, and can be determined from experimental evidence about change of concentration with time, summarized in graph form.

Consider again the graph in figure 2, but with the sections for equivalent time intervals drawn as straight lines.

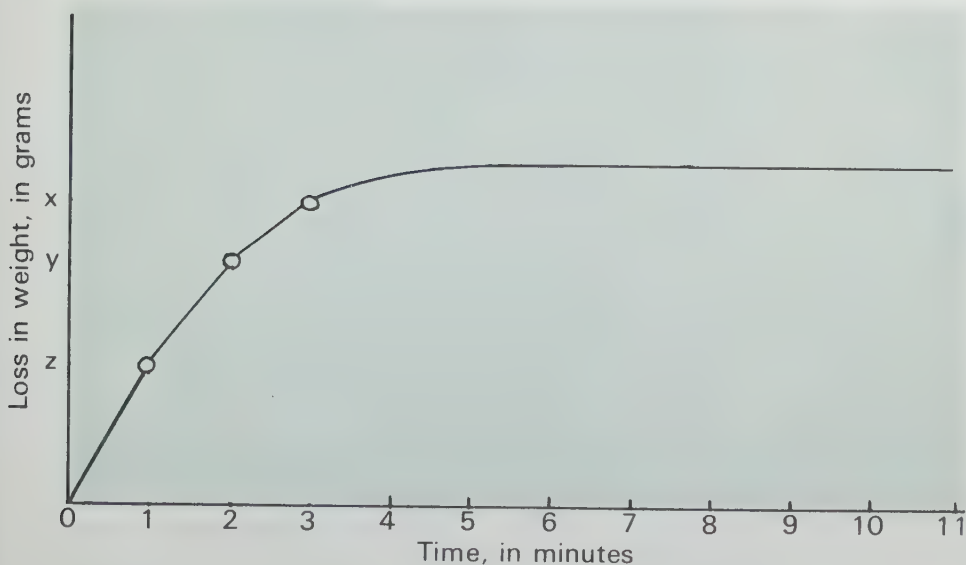


Figure 3

Which is the steepest of these lines? The first. When the gradient is steepest the reaction is fastest, so that there is no gradient at all when the reaction is complete. For the graphs of concentration changes against time, the steepness of the curve is an indication of the rate.

The specific rate, that is, the rate at a given time, is obtained by determining the steepness of the curve at the time interval required. Steepness, or slope, is determined by drawing a tangent to the curve at the required point in time. This technique is best illustrated by another example.

The pyrolysis, that is, decomposition by heat, of acetaldehyde at 500°C gives carbon dioxide and methane, and is a fairly slow reaction.



Because one mole of acetaldehyde gives 2 moles of products, there is an increase in pressure as the reaction proceeds, if the volume is kept constant. To achieve this the acetaldehyde is placed in a closed container fitted with a pressure gauge, and then the con-

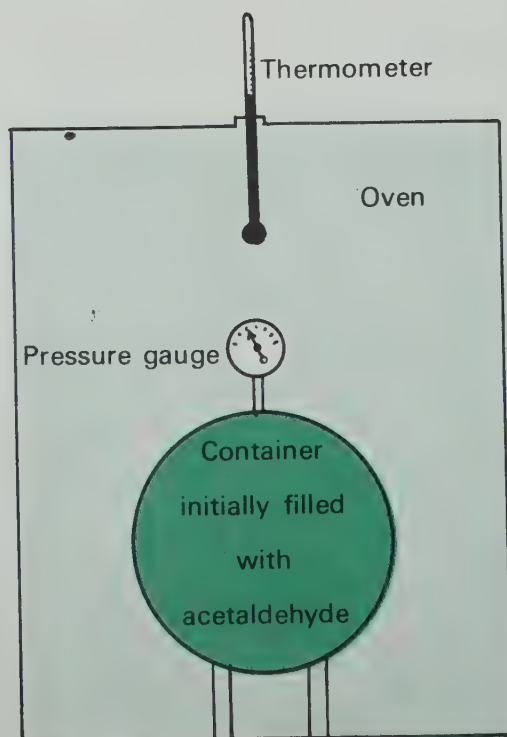


Figure 4

tainer is brought to the required temperature. The increase in pressure observed is related to the increase in concentration of products, so, experimentally, the reaction is an easy one to follow—the readings are just taken from the gauge.

Typical results for the pyrolysis of acetaldehyde vapour at 520°C are indicated in figure 5.

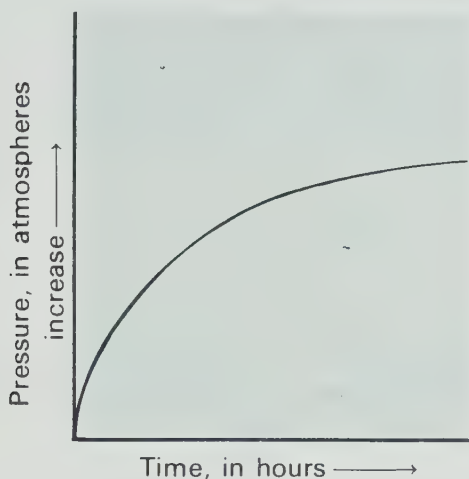


Figure 5

During the first hour the pressure changes are most marked; during subsequent hours the net pressure changes are less marked.

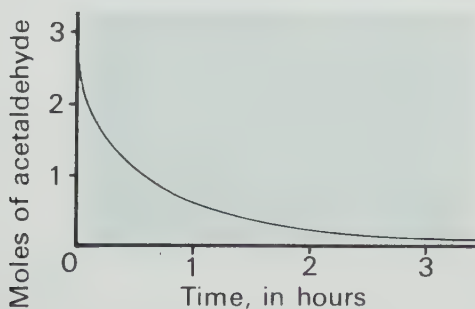


Figure 6

For specific rate, the graph of concentration against time is required. From the observed pressure changes, concentration changes can be determined and the required graph drawn. The rate at a given time t (a specific rate) is given by the slope of the curve at this time. The tangent to the curve at time t is drawn and extended to cut both axes.

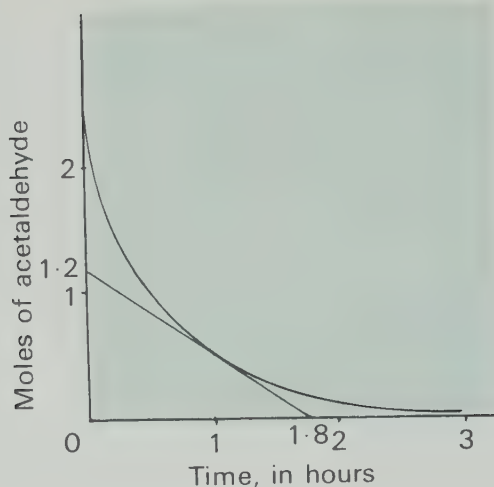


Figure 7

This tangent then gives a concentration change (ΔC) from the vertical axis and a time change (Δt) from the horizontal axis, and the required

$$\text{reaction rate} = \frac{\Delta C}{\Delta t}$$

PROBLEM

Determine, from the given graph summarizing the observed concentration changes of acetaldehyde, the specific rate for a pyrolysis of acetaldehyde after 1 hour's decomposition.

Solution

The tangent at $t = 1$ hour is drawn and extended to cut both axes.

At this time $\Delta C = 1.2$ moles and Δt 1.8 hours

$$\begin{aligned} \therefore \text{rate} &= \frac{1.2}{1.8} \text{ moles hour}^{-1} \\ &= \underline{0.67 \text{ moles hour}^{-1} \text{ of acetaldehyde}} \end{aligned}$$

Another example studies the decomposition of dinitrogen pentoxide (N_2O_5).

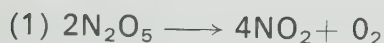
PROBLEM

The change of concentration of N_2O_5 during its decomposition into NO_2 and O_2 was studied and the following data obtained.

t (in minutes)	$[\text{N}_2\text{O}_5]$
0	4
1.5	3.4
3.0	3.1
4.5	2.8
9.0	2.4
13.5	1.9
20.25	1.3
27.0	0.9

- (1) Write an equation for the decomposition.
- (2) Plot the graph $[\text{N}_2\text{O}_5]$ against time.
- (3) Calculate the rate in terms of $[\text{N}_2\text{O}_5]$ at $t = 10$ minutes.

Answers



(2)

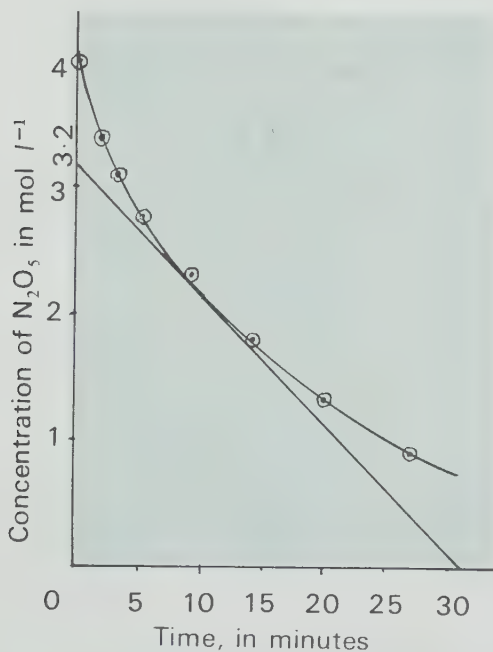


Figure 8

- (3) The tangent at $t = 10$ minutes cuts both axes such that
 (i) $[\text{N}_2\text{O}_5] = 3.2\text{M}$ and (ii) $t = 31$ minutes, therefore

$$\text{specific rate} = \frac{3.2 \text{ mol l}^{-1}}{31 \text{ minutes}}$$

$$= 0.1 \text{ mol l}^{-1} \text{ min}^{-1} \text{ of dinitrogen pentoxide}$$

More information about changing rate will be given on page 28.

How Are Concentration Changes Measured?

An ever-present problem facing research and analytical chemists is the accurate measurement of concentration changes. This measurement of concentration changes is an example of quantitative analysis. (If you have trouble remembering the difference between quantitative and qualitative, think of quantity—that is, ‘how much’, and quality—that is ‘what kind’.)

The increasing use of instruments which enable chemists to measure concentration changes quickly and precisely has helped considerably in the study of reaction rates. For some scientists this development of instrumental analysis is one of the most important aspects of recent chemical progress. The work of reaction rate chemists involves the practical problem of determining changes in concentration of a reactant or a product, at a given temperature, over a suitable time interval.

Some of the methods of doing this are considered below but a full understanding of these methods is not a necessary prerequisite for mastering reaction rate concepts.

Chromatography

During the past twenty-five years **chromatography** has become one of the major research and practical analytical techniques available to chemists. The word chromatography comes from the Greek *chroma*—colour, and literally means colour writing, because the early techniques involved separation according to colour. Chromatography is a technique for separation, purification and identification; it is used today for both coloured substances and colourless substances, and for gaseous mixtures as well as solution analysis. The principle involved is the same for both gas and solution analysis. It might be described as an **adsorption/desorption** process. It is important to know what adsorption means. Adsorption is not the same as absorption. Adsorption is a surface phenomenon, the holding of one substance in the surface of another; absorption means the penetration of one substance into another, for example, ink into blotting paper.

Components in a mixture are adsorbed on to a suitable medium and then released (desorbed). Since the rate of adsorption/desorption is different for different substances, separation of even extremely complex mixtures becomes possible. Some subdivisions of chromatographic techniques are:

Adsorption Chromatography

Here adsorption/desorption takes place on a finely divided solid, usually supported in a column. The separation is brought about by some components in the mixture being adsorbed, for some length of time, by the column material. The extent of adsorption is usually related directly to the polarity of the compound; that is, the more polar a substance, the more it is adsorbed.

A vertical glass tube is packed with a column of adsorbent. Calcium carbonate, calcium sulphate or aluminium oxide, all in



Figure 9(a). A simple demonstration of the selective adsorption is the use of a piece of chalk to separate the dyes contained in coloured inks, left to right, black ink, blue ink, red ink, white chalk

powdered form, are common adsorbents. A solution of the mixture, the components of which are to be separated, is poured on to the column. The best solvent used to dissolve a mixture is determined by experiment. The mixture is then washed or *eluted* through the column by adding more solvent. The solvent is usually called the *eluting solution*, and the process of washing is called *elution*.



Figure 9(b). Apparatus used for chalk chromatography, showing a petri dish containing the solution and beakers containing the inks

Consider a mixture of A and B. A is more polar than B.

As this mixture is washed or eluted through the column by the eluting solution, the more polar A, being more firmly adsorbed, is held back on to the column material so that the first wash contains B. Continued eluting then brings out A.

Chromatography was discovered by the Russian-born chemist-botanist Tswett in 1903. He was experimenting with the pigment chlorophyll and he described his technique thus:

When a petroleum ether solution is filtered through a column of adsorbent (I use mainly calcium carbonate which is tamped firmly into a narrow glass tube), the pigments are resolved, according to the adsorption sequence, from top to bottom into various coloured zones. The more strongly adsorbed pigments displace the more weakly adsorbed ones and force them further downward.



Figure 10. Apparatus used for column chromatography showing the glass column with the eluting solvent passing through the adsorbent material which is coloured by the solution of the mixture to be separated

This separation becomes practically complete when, after the pigment solution has flowed through, one passes a stream of pure solvent through the absorbent column. Like light rays in the spectrum, the

different components of a pigment mixture, obeying a law, separate on to the calcium carbonate column and can thus be qualitatively and quantitatively determined. I call such a preparation a chromatogram, and the corresponding method, the chromatographic method.

It is self-evident that the adsorption phenomena described are not restricted to the chlorophyll pigments and one must assume that all kinds of coloured and colourless chemical compounds are subject to the same laws.

Although well described, this technique was not used again by chemists until some 40 years later. How many similar discoveries are waiting to be developed?

Paper Chromatography

Because it is a simple technique, paper chromatography is extensively used. The name tells how the separation is carried out, namely on paper; ordinary filter paper is the most commonly used material.

The principle is the same as for adsorption chromatography. Water molecules are present in the paper and these are linked to the cellulose fibres of the paper. These water molecules act as the stationary part, like the solid adsorbent in column chromato-

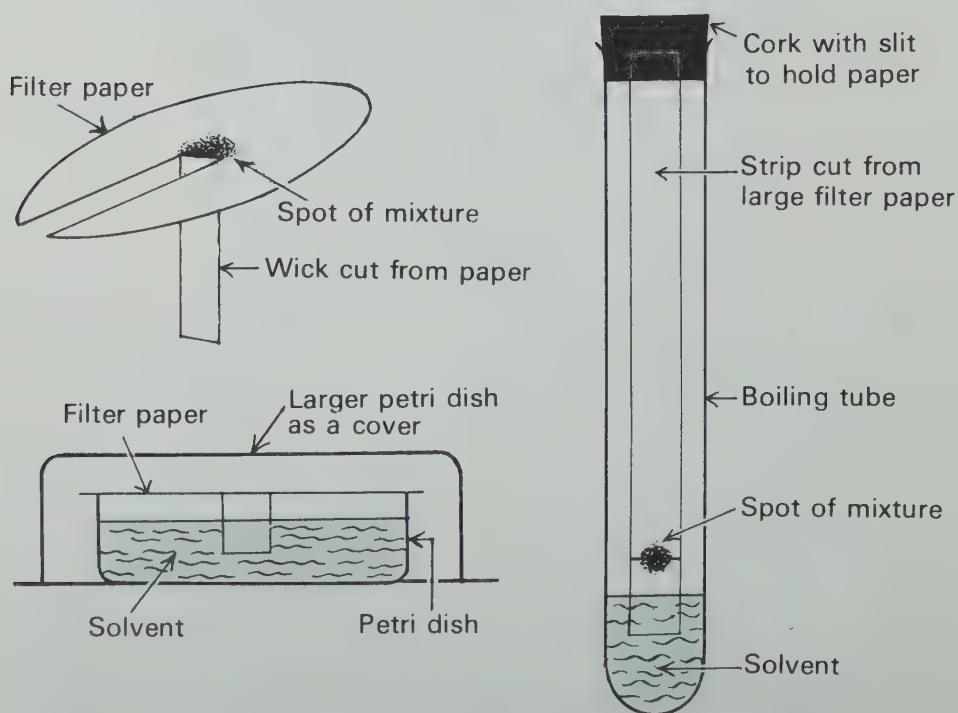


Figure 11. Apparatus used for paper chromatography

graphy, and hold back polar substances more than non-polar substances. The eluting solvent is usually brought through the paper by capillary action.

Paper chromatography is most suited when only very small quantities are available. Forensic science uses paper chromatography for the identification of poisons and drugs, and extremely small quantities of these materials can be accurately identified. Health authorities use chromatographic techniques to detect trace quantities of illegal dyes, preservatives or flavourings which may have been added to foodstuffs.



*Figure 12. Paper chromatography of dyes in ink, (i) blue ink, (ii) red ink, (iii) black ink, (iv) green ink. Solvent: *n*-butanol, ethanol, 2*M* ammonia (60:20:20 by volume).*

Many advances in medicine have been made through the use of chromatography, including paper chromatography. For example, some eighty related compounds have been found in urine by using chromatographic separating techniques. The compounds are called steroids.

Gas Chromatography

This technique is used for analysis of gaseous substances. It can be used for liquids and solids, provided they can be volatilized (vaporized) without decomposition. The sample to be analysed is injected into the apparatus and moves by means of a carrier gas (usually nitrogen because it is inert) through the adsorbent which is packed in a column. The oil refining industry uses gas chromatography extensively. Samples are taken at various stages during the refining process and analysed. Hence the quality of their products is controlled.

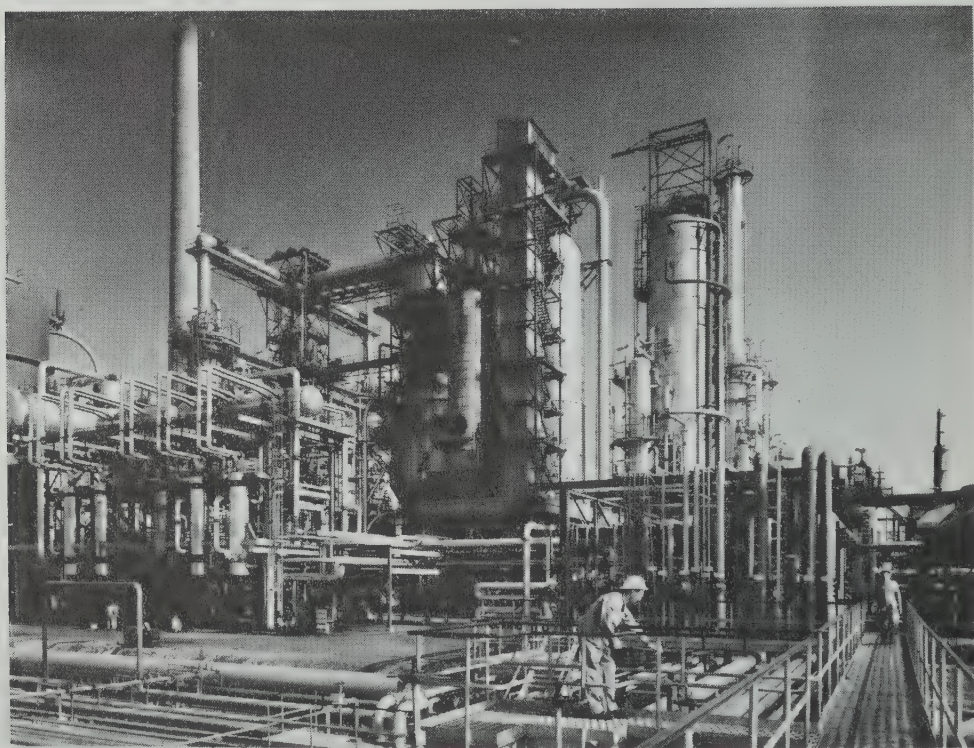


Figure 13. The catalytic cracking unit at Shell's oil refinery in Sydney

Because of selective adsorption, the components of the mixture emerge at definite intervals from the column and are detected.

Sophisticated commercial apparatus, such as that at oil refineries incorporates devices for measuring the thermal conductivity of the various components and plots this information automatically on graphs. These and similar graphs, giving percentage of components are called chromatograms.

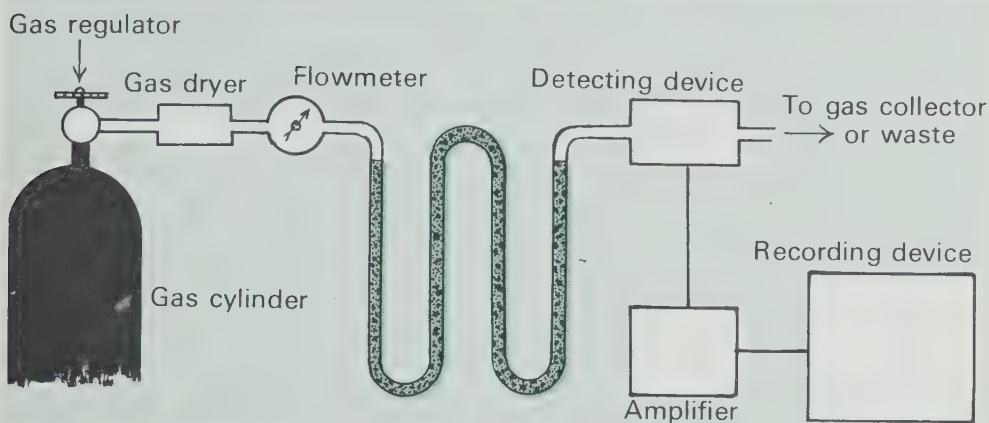


Figure 14. Outline of apparatus used for gas chromatography

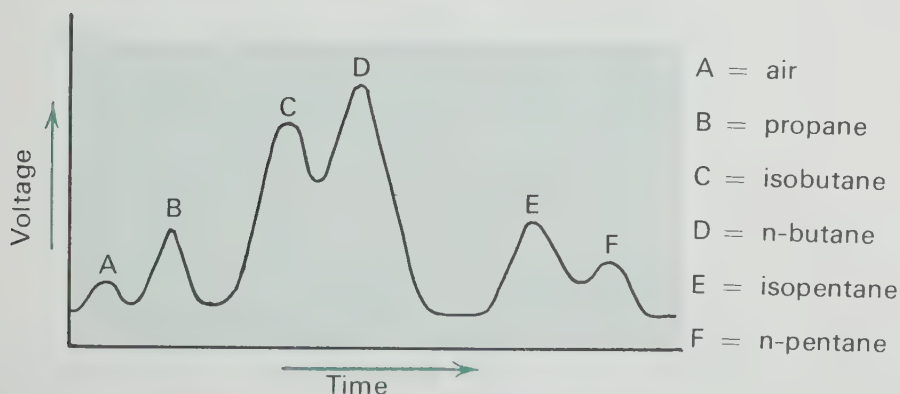


Figure 15. Chromatogram showing the separation of gases from crude petroleum on alumina using hydrogen as the carrier gas

Chemical Analysis

Chemical analysis may be used to determine concentration changes. Some chemical analysis techniques are:

(1) Volumetric Analysis

This is analysis of volume concentration by chemical reaction as in acid-base titrations.

For reaction rate studies, an analysis is made of samples periodically withdrawn from the reaction mixture at the required time intervals. This determines how the concentration changes. An example of this procedure is given by the hydrolysis of the ester, ethyl acetate. Ethyl acetate is hydrolysed by water to give acetic acid and ethyl alcohol.



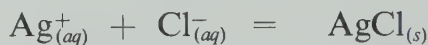
A measure of the increase in concentration of acetic acid can be used to determine the rate. The acid produced may be titrated against a standard alkali solution to determine its concentration. However, precautions must be taken to prevent further reaction occurring while the analysis is being made. In ester hydrolysis the samples are immediately diluted to prevent further hydrolysis. With some reactions it is particularly difficult to prevent the reaction continuing whilst measurements are made.

(2) Gravimetric Analysis

If an insoluble substance can be precipitated from the reaction mixture, gravimetric analysis is used to determine the original concentration. An example of this is the hydrolysis by alkali of an alkyl halide to give the corresponding alcohol and aqueous chloride.



Addition of Ag^+ ion will precipitate the Cl^- ion as insoluble silver chloride.



This insoluble substance is filtered off, dried and weighed. The fraction of Cl^- ion making up the total weight is calculated, and thus the concentration of Cl^- ion originally present may be determined.

Physical Analysis

If a change in a physical property is related to a reactant's concentration, such variations in physical properties are a useful means of measuring the concentration changes.

(1) Pressure Changes

In gaseous reactions, where the number of moles initially present

changes during the course of the reaction, the resulting changes in pressure can be used to determine concentration changes.

Consider



The concentration of NO_2 is directly related to the increase in pressure if the reaction rate is being studied at constant volume.

(2) Other Properties

These include colour intensity changes, density changes, and electrical conductivity changes. These may be used as an indirect measure of concentration changes, provided that instruments of sufficient accuracy are available to measure these physical changes. Colour intensity changes are the simplest to measure, and the instrument need be no more than a device which allows the eye to compare a standard colour representing a known concentration, with the colour of the unknown. The concentration of chlorine in swimming pools is determined by this colour matching method, and the concentration of hydrogen ions as a measure of the acidity of solutions is also determined by colour matching, using a universal indicator or pH papers.

Chemists prefer using physical methods rather than chemical methods for measuring concentration changes and for determining reaction rates. Chemical methods usually disturb the course of a reaction by increasing the volume or by removing some of the reactants and/or products, from the reaction mixture.

Heterogeneous and Homogeneous Reactions

Generally the reaction rates studied will be for **homogeneous** (Greek *homos*—same, and *genos*—kind) reactions, that is, reactions in which the reactants, and in most cases the products, are in the same physical state. Reactions where the reactants are in different physical states are termed **heterogeneous** (Greek *heteres*—other). The reaction between magnesium and dilute hydrochloric acid is an example of a heterogeneous reaction.

Two complications arise in the study of reaction rates for heterogeneous reactions involving the solid state.

These are:

- (1) The surface area of the solid influences the rate of reaction. A mixture of coal dust and air can explode, whereas lumps of coal burn comfortably in air. It is practically impossible to

measure the exposed surface area of a solid; hence controlled conditions for the study of heterogeneous reactions are practically impossible to maintain. Some of the early coal-carrying ships were lost at sea because it was not realized that coal dust and air could explode.

- (2) The concentration changes occur at the boundary where the reaction is proceeding and not throughout the total reaction environment. This makes such changes difficult to measure.

There are no fundamental chemical differences between homogeneous and heterogeneous reactions. Homogeneous reactions are easier to study, and therefore are used extensively in this booklet.

Factors Affecting Reaction Rates

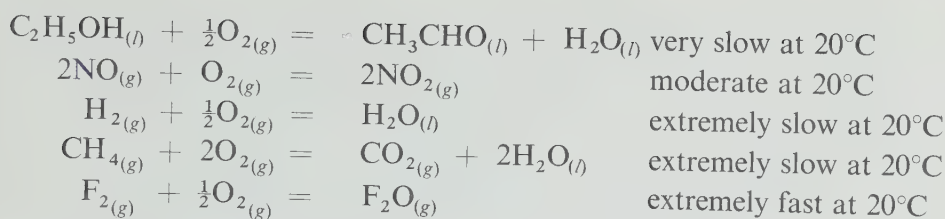
What are the factors affecting reaction rates?

You must have observed reactions that have not worked well, or have not worked at all! (The latter usually happens during a class demonstration—to the embarrassment of one, and to the amusement of many!) Why does this happen? The polite answer is that conditions have been varied, albeit unknowingly, from those most desirable. What then are these conditions that affect the rates of reaction? Laboratory observations over a long term have shown that there are four. They are:

- (a) nature of reactants,
- (b) concentration of reactants,
- (c) temperature, and
- (d) catalysis.

Nature of Reactants

It is a fact of chemistry that some reactions are fast, while others are slow. Can any predictions be made about reactions and their rate, by inspection? Consider the following reactions involving oxygen at room temperature:



All the above reactions involve oxygen, yet there is a wide variation in reaction rate. A possible conclusion is that the difference in rates is due to the nature of the other reactant. The nature of the reactants as a factor in determining the speed of a chemical reaction has been recognized, if not explicitly stated, since chemistry was first studied by the alchemists. However, no explanations were given until reactions were described in terms of the atomic nature of matter about fifty years ago by an American chemist, Gilbert Lewis, and more recently by another American chemist, Linus Pauling—the 1954 Nobel Prize winner in chemistry ‘for his research into the nature of the chemical bond’. But prediction of rates, although at times fairly haphazard, is being made more reliable as we gain more knowledge of the way in which atoms make and break bonds with other atoms. This study of the way, or mechanism, by which a reaction occurs, and the rate of re-reaction, is called **chemical kinetics**. Chemical kinetics make the following predictions:

- (a) Reactions between ions which combine in a mole-to-mole ratio are almost instantaneous.

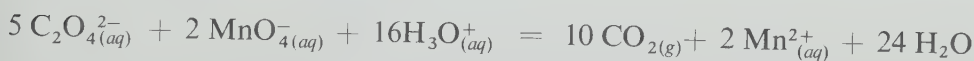
For example:



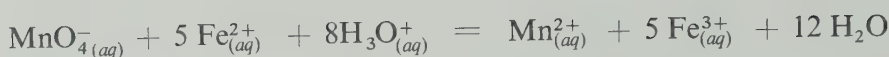
Both these reactions have a simple mechanism; contact between oppositely charged ions is sufficient for reaction to occur.

- (b) Reactions between complex ions are usually slower than those between simple ions.

For example, the reaction



is quite slow at room temperatures. This is not unexpected. The reaction looks more complicated and probably is; it will therefore take longer. But inspection is not always a valid guide. The oxidation of the iron II ion ($\text{Fe}_{(aq)}^{2+}$) to the iron III ion ($\text{Fe}_{(aq)}^{3+}$) by acidified permanganate solution looks like a complicated reaction yet is quite fast!



(c) Reactions involving molecules are generally slower than reactions between ions at room temperature.

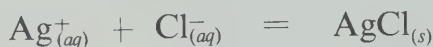
For example, the burning of octane with oxygen



is, fortunately, extremely slow at room temperatures.

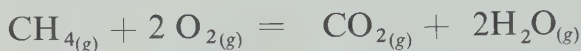
A study of how these reactions occur, that is of their reaction mechanisms, shows that:

(i) Reactions not requiring bond rearrangements, for example,



are usually rapid, and

(ii) reactions involving breaking of bonds, and forming of new bonds, for example



are usually slow unless the temperature is high.

Prediction (i) is often more reliable than prediction (ii).

Because our predictions are not always accurate, there is obviously much more to be learnt about how reactions take place. To simplify this study, one reaction at a time will be considered. This means that the nature of the reactants becomes a constant and the other changes—concentration changes, temperature changes, and introduction of catalysts—are considered for each reaction.

Concentration Changes

It has been found by experiment that the rate of a homogeneous chemical reaction depends on the concentration of the reactants.

Consider a simple example. Hydrogen peroxide in an alkaline solution decomposes to give water and oxygen. The graph, consolidating the practical results from the study of this decomposition, shows the variation of concentration with time.

As the steepness of the curve is a measure of the reaction rate, this graph shows that the reaction was comparatively fast initially, but as the concentration of the hydrogen peroxide decreased the reaction slowed down.

From this experiment, and of course many others, it has been possible to reach the general conclusion that an increase in the

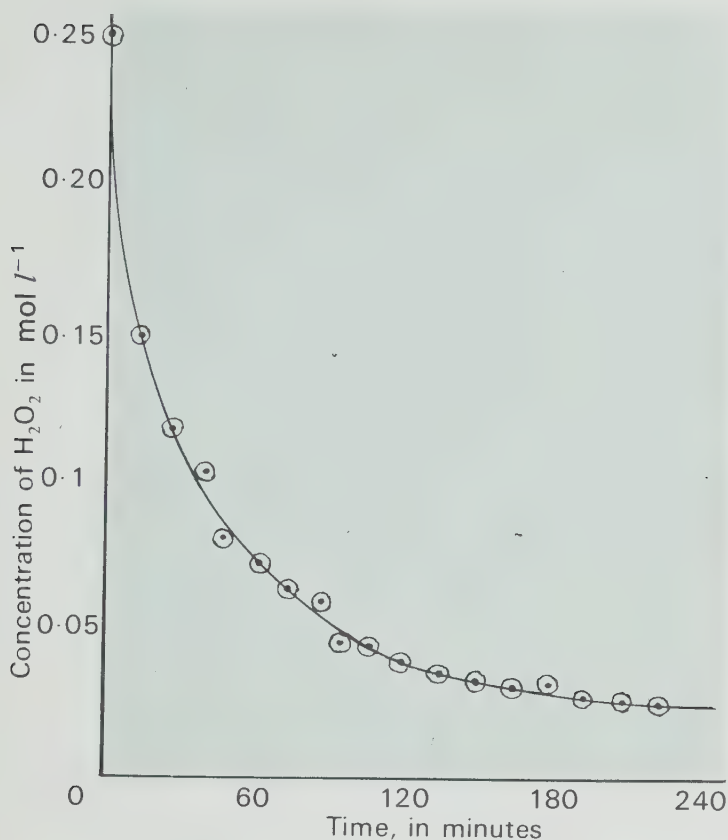
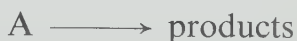


Figure 16

concentration of a reactant increases the rate of a reaction, or a decrease in the concentration decreases the rate of a reaction.

But the question now becomes: is there a simple relationship between the rate of a reaction and the concentrations of the reactants?

Consider a reaction where a single species is reacting to form new products



It may be a decomposition reaction such as



or it may be a dimerization reaction such as



Analysis of the results obtained from rate studies of reactions of this type show that frequently it is possible to summarize the

experimental findings by the statement—the rate of the reaction is proportional to the concentration of the reaction raised to some power.

$$\text{Rate} \propto [\text{A}]^n$$

Introduction of a constant to change the proportion into an equality gives

$$\text{Rate} = k[\text{A}]^n$$

Where k is called the specific rate constant or, more often, simply the **rate constant**,
 n is called the order of the reaction.

A value of $n = 0$, called **zero order**, means that the rate of a reaction is independent of the concentration of A. Such reactions are known. For example, reactions catalysed at metal surfaces are sometimes of this type and are called zero order reactions.

A value of $n = 1$, called **first order**, means that the rate of a reaction is proportional to the concentration of A, $[\text{A}]^1$.

$$\text{R} = k[\text{A}]^1$$

A value of $n = 2$, called **second order**, means that the rate of a reaction is proportional to the square of the concentration of A, $[\text{A}]^2$.

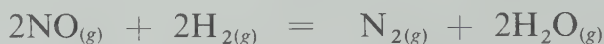
$$\text{Rate} = k[\text{A}]^2$$

The reaction is said to be second order with respect to A.

Consider the more complicated reaction between A and B:



As an example of this type of reaction consider the reduction of nitric oxide by hydrogen, in the gaseous phase:



The rate for this reaction is fairly readily determined by observing the changes in pressure during the reaction if the reaction is carried out in a closed container.

Because 4 moles of reactants give only 3 moles of products, the reaction has gone to completion when a 25% reduction in initial pressure is obtained.

Two series of experiments are made. In the first the initial concentration of nitric oxide is kept constant whilst the initial concentration of hydrogen is altered. In the second series the initial

concentration of hydrogen is kept constant but the $[\text{NO}]$ is altered.

EXPERIMENT A

Initial $[\text{NO}]$ Constant—varying $[\text{H}_2]$ —constant temperature

Results

Experiment No.	$[\text{NO}]$	$[\text{H}_2]$	Rate (R) $\text{mol l}^{-1} \text{min}^{-1}$
1	constant	1	6
2	constant	2	12
3	constant	3	18

Thus, when the $[\text{H}_2]$ was increased 2 times, as in experiment 2, the rate was observed to increase by a factor of 2. When $[\text{H}_2]$ was increased to 3 times that used in the first experiment the rate was observed to increase by a factor of 3.

These results can be expressed:

$$R \propto [\text{H}_2]^1 \quad ([\text{NO}] \text{ constant; temp. constant})$$

EXPERIMENT B

Initial $[\text{H}_2]$ constant — varying $[\text{NO}]$ — constant temperature

Results

Experiment No.	$[\text{NO}]$	$[\text{H}_2]$	Rate $\text{mol l}^{-1} \text{min}^{-1}$
1	1	constant	2
2	2	constant	8
3	3	constant	18

The relationship between the changes in concentration of NO and the observed rate are not at first apparent. It is a proportionality involving the square of the concentration, $[\text{NO}]^2$. When the $[\text{NO}]$ is doubled, the rate is increased 4 times. When the $[\text{NO}]$ is tripled the rate is increased 9 times.

The results can be expressed:

$$R \propto [\text{NO}]^2 \quad ([\text{H}_2]^1 \text{ constant; temp. constant})$$

Thus if $R \propto [\text{H}_2]^1$ and also $\propto [\text{NO}]^2$ it is proportional to the product $[\text{H}_2]^1 \cdot [\text{NO}]^2$ when both concentrations are changed.

$$\begin{aligned} \text{i.e., } R &\propto [\text{H}]^1 \cdot [\text{NO}]^2 \\ \therefore R &= k [\text{H}]^1 \cdot [\text{NO}]^2 \end{aligned}$$

This particular expression is called the **rate equation** for this reaction.

The **rate equation** is an expression describing the rate of a particular reaction in terms of the concentration, usually molar concentrations, of each reacting substance.

A general expression for the rate equation is:

$$R = k [A]^n \cdot [B]^m \dots$$

where n and m are the appropriate powers to which $[A]$ and $[B]$ must be raised to coincide with the determined experimental data, and the dots, \dots , represent other reactants which may be involved.

In this general expression for the rate equation:

n is the order of the reaction with respect to the reactant A,

m is the order of the reaction with respect to the reactant B.

$(n + m)$ is called the overall order of the reaction.

For the reduction of nitric oxide by hydrogen, it is found that the reaction is:

- *first order with respect to hydrogen*
- *second order with respect to nitric oxide*
- *an overall third order reaction*

Note that the orders of this reaction are not identical with the stoichiometrical coefficients of the balanced equation,



It must be stressed that the rate equation is determined by experiment and cannot be predicted from an inspection of the balanced equation.

The decomposition of dinitrogen pentoxide (N_2O_5) is usually represented by the equation



From experimental evidence the rate equation for this reaction is

$$R = k[\text{N}_2\text{O}_5]^1$$

This reaction is first order with respect to N_2O_5 .

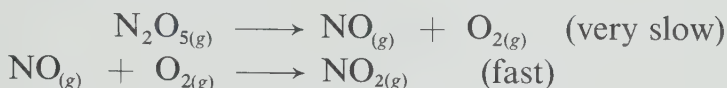
The disparity between the order of the reaction and the stoichiometrical coefficients is because the balanced equation is simply an overall statement of what happens and does not indicate the path by which the process occurs. There may be several intermediate steps in the reaction pathway and, if one of these steps

is very much slower than the other steps, the observed rate will be essentially the rate of this slow step.

For example, if the reaction



were to proceed by the steps



then this would explain the overall first order which has been found experimentally.

If the intermediate steps all proceed at approximately the same rate the overall observed rate will be a complicated mixture of the rates of the intermediate steps. The series of intermediate processes, or steps, which is postulated as the pathway by which a reaction proceeds is called the **'mechanism of a reaction'**.

Temperature Changes



Figure 17. Frozen food storage. It is not being frozen that preserves food—it is the low temperatures. At -20°C the reactions involved in food deterioration are extremely slow. Therefore frozen foods in the home should only be kept in refrigerators designed to produce these lower temperatures

How does temperature affect the rate of a chemical reaction?

Chemical evidence and your own experience show that temperature has a marked effect on reaction rates. Increase in temperature increases the rate of reaction, and the converse also applies. This observation is well demonstrated in the home, where the stove is used to increase the rate of the reactions involved in cooking, while the refrigerator decreases the rate of the reactions involved in food decomposition.

It must be stressed that the rate for both endothermic and exothermic reactions is increased with increase of temperature and decreased with decrease in temperature.

It is the rate constant k that is changed with changes in temperature. k is increased with increase of temperature and decreased with decrease of temperature. The amount of the variation in k varies from one reaction to another, but as a rough guide k often doubles in value for every 10°C rise in temperature.

This is a much greater effect than is often appreciated. For a 100°C change in temperature the rate will be twice as great for the first ten degree rise, 4 times as great for the first twenty degree rise and therefore for a hundred degree rise the rate increase will be:

$$\begin{aligned} 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \\ = 2^{10} \\ = 1024 \text{ times greater.} \end{aligned}$$

One problem, as yet to be answered, presents itself to the thinking chemistry student—why does temperature have such a marked effect on reaction rate? This will be discussed later.

Catalysis

Ask an industrial chemist, 'What area of research is likely to produce the most significant developments for the chemical industry?' and there is a good chance that his answer would be 'catalysis'. It is probably true to say that the future of the chemical industry is bound up with the development of suitable catalysts. Industry has to satisfy ever-increasing demands for new materials in commercial quantities, be these drugs, dyes, plastics or heat shields for supersonic aircraft and spacecraft.

Catalysts are needed for increasing reaction rate at lower temperatures and pressures since lower temperatures and pressures mean lower production costs and, generally, more effective

control. They are also used for singling out for attack particular substances from complex mixtures. Yet the strange thing is that we are constantly surrounded by hundreds of catalysts which do just these things. These catalysts are the **enzymes** which operate in practically every chemical process in all living things.

What are catalysts?

The name *catalyst* was given to chemistry by a Swedish chemist, J. J. Berzelius, in 1835. (It is from the Greek and literally means 'to loosen'.) A German chemist, W. Oswald, in 1902 defined catalysts as substances whose presence alters the reaction rate for a reaction, but which can be recovered unchanged at the completion of the reaction. He used the term *catalysis* to describe the effect of catalysts. This definition does not offer any explanation of how catalysts work, nor did Oswald offer any explanation.

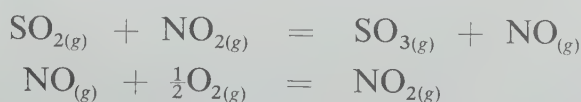
Catalysts must play some part in a reaction even though their recovery unchanged at the end of the reaction gives the impression that they do not. If they were not involved in the reaction then they could hardly change the rate!

Firstly, some catalysis terminology.

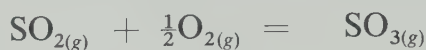
A **negative catalyst** is one which slows down a reaction. An example is the use of tetraethyl lead (T.E.L.), in petrols. A petrol air mixture explodes. A steady burning rather than an explosion is more efficient in the internal combustion engine because this increases performance and engine life. The addition of small quantities of tetraethyl lead ($\text{Pb}(\text{C}_2\text{H}_5)_4$), slows down the petrol air reaction, but increases air pollution.

A **positive catalyst** increases reaction rate. The terms *homogeneous* and *heterogeneous* are used to describe the state (i.e., solid, liquid or gaseous) of the catalyst in relation to the state of reactants. If the catalyst is of the same state as reactants, it is termed a homogeneous catalyst. An example of a homogeneous catalyst is nitrogen dioxide in the oxidation of sulphur dioxide to sulphur trioxide—all are gases.

The following reactions show the part that this catalyst plays. The reactions, very much simplified, can be represented:



The overall reaction can be represented by



An intermediate compound, namely nitric oxide, is formed by the catalyst, and the formation of such intermediate compounds is typical of homogeneous catalysis.

An example of a heterogeneous catalyst is the use of platinum to catalyse the reaction between hydrogen and oxygen. Hydrogen and oxygen react extremely slowly at room temperature. Insertion of platinum causes the reaction to take place on the surface of the catalyst, resulting in a rise of temperature in the platinum. As the platinum gets hotter, the reaction rate increases until it is so fast that an explosion results. A corollary here is that surface condition has a significant effect on catalytic activity of heterogeneous catalysts.

The reaction is catalysed because the surface platinum atoms are able to adsorb oxygen atoms.

High energy oxygen molecules strike the metal surface, dissociate into atoms, and are held.

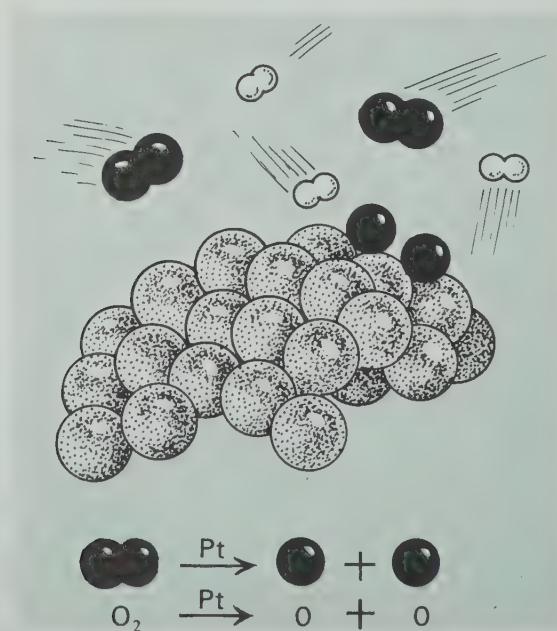


Figure 18

When hydrogen molecules strike the oxygen atoms, they com-

bine with them, and remove them from the surface of the catalyst. The surface can now accommodate other oxygen atoms.

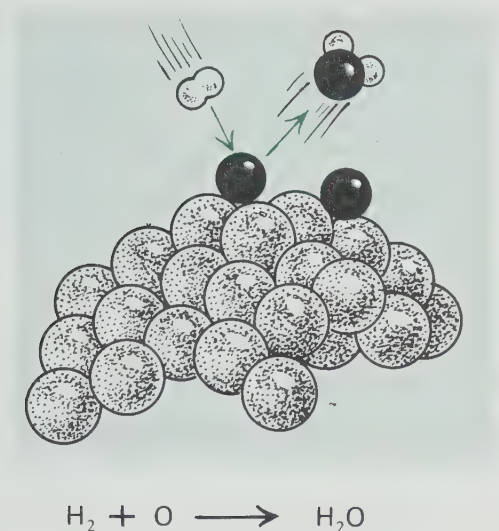


Figure 19

As the energy of this reaction is released, so the reaction rate increases until an explosion results.

An example of a heterogeneous catalyst used in the home is the flameless igniter for lighting gas appliances. Industry uses catalysts extensively. Silver for catalysing the reaction between methanol and oxygen for making formaldehyde; vanadium pent-oxide in making sulphuric acid; nickel in making petroleum products; and platinum rhodium alloy for catalysing the reaction between ammonia and oxygen in the manufacture of nitric acid—are just a few of countless examples.

The importance of catalysts to biological systems cannot be overstressed. These catalysts—complex organic substances produced by the living organism—are termed *enzymes* (from the Greek, meaning ‘in yeast’). Enzymes change inherently slow biochemical reactions into faster reactions, making them more useful to the organism.

Enzymes control digestion of food, photosynthesis in plants, fermentation processes in beer and wine making: in fact all living processes. We depend upon enzymes for life!

How enzymes catalyse reactions is not fully understood but, like other catalysts, they probably form intermediate complexes.

The shape of a particular enzyme enables it to fit close to its reacting molecule and form a complex.

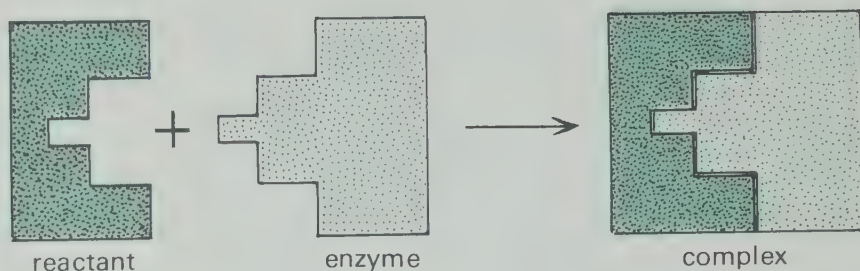


Figure 20

This idea is often loosely described as the 'key and lock' theory. Only one type of key is supposed to fit a particular lock, and so only one type of enzyme is able to fit a reactant molecule. This explains the specific nature of enzyme catalysis, as it is known that only one enzyme will catalyse one particular reaction.

Since the complex formed in the above reaction is unstable, decomposition occurs, yielding the original enzyme, and products formed from the reactant.

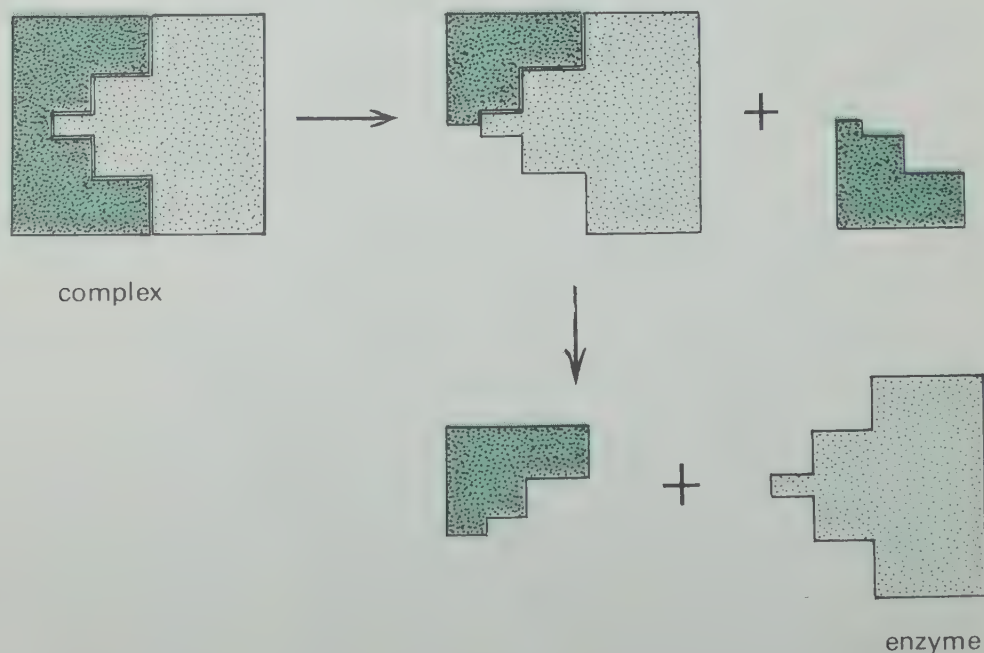


Figure 21

Because of the specific nature of enzymes, it is necessary for living cells to produce a different enzyme for each of the many hundreds of different chemical reactions required to sustain life. It is likely that the rapid growth of cancer cells involves catalytic activity. If a way could be found of blocking-out the enzyme or enzymes responsible for the rapid reproduction of cells, then it is probable that cancer could be controlled. This approach is being studied in cancer research.

The Collision Theory for Reaction Rates

Concentration Considerations

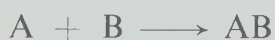
So far the observed facts of reaction rates have been discussed without much theoretical interpretation. The collision theory partially succeeds in explaining these observations. This theory makes the assumption that, for reaction to occur, the reacting species must collide, or at least come close together.

How can reaction rate be related to collisions? Two more reasonable assumptions can be made:

- (a) the greater the number of collisions, the faster the rate, and
- (b) the greater the number of collisions that result in a reaction, then the faster the rate.

Again—fairly realistic?

If the rate of reaction is dependent on the number of collisions, then it should be possible to relate concentration to rate. For this study a simple 'one-step' reaction will be used. Molecule A reacts with molecule B to produce molecule AB.



Now the collision theory postulates that the rate of formation of AB is proportional to the frequency of collision between A and B. How is the collision between A and B related to their concentration?

Consider the following hypothetical situations:

BOX I: contains 1 molecule of A and 1 molecule of B.

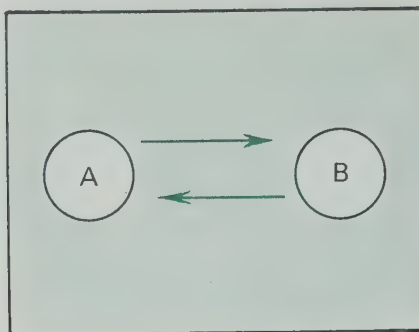


Figure 22. Box I

Over a period of time the chances are that there will be one collision between molecules A and B.

BOX II: contains 2 molecules of A and 1 molecule of B.

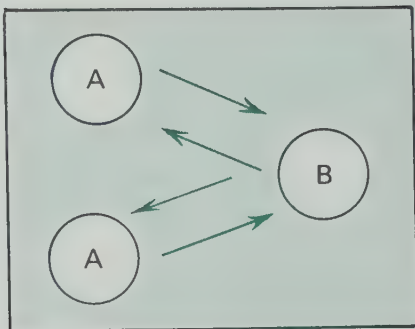


Figure 23. Box II

Now for the same time interval as considered for Box I, where there was the chance of one collision, the chances are that there will be two collisions between A and B because there are twice as many A molecules present in Box II.

BOX III: contains 2 molecules of A and 2 molecules of B.

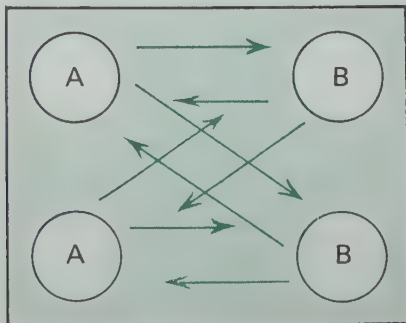


Figure 24. Box III

What are the chances of collisions between A and B over the same time interval as before? The chances have been increased 4 times because there are twice as many A molecules and twice as many B molecules in Box III as in Box I.

A pattern is developing. The chance of collision is proportional to the number of molecules present (that is, to their concentration) and if rate of reaction is dependent on collisions, it can be expressed thus:

$R \propto n_A$ where n_A = number of moles of A present
and $R \propto n_B$ where n_B = number of moles of B present

$$\therefore R \propto n_A \cdot n_B$$

but $n_A \propto [A]$ (in mol l^{-1})

and $n_B \propto [B]$ (in mol l^{-1})

$$\therefore R \propto [A] \cdot [B]$$

$$\therefore R = k [A] \cdot [B]$$

Consider the reaction represented by



and try out the above 'box argument'. The results will be similar to those already obtained,

$$R \propto n_A \cdot n_A$$

$$\text{i.e., } R \propto [A] \cdot [A]$$

$$\therefore R = k[A] \cdot [A]$$

$$\text{i.e., } R = k[A]^2$$

This kind of reasoning can be developed such that the rate expression for a general reaction represented by:



becomes:

$$R \propto [A]^m \cdot [B]^p \cdot [C]^q$$

Thus the coefficient in the balanced chemical equation describing the reaction becomes the exponent in the expression of rate.

But this reasoning is another example of the old adage, 'A little knowledge is a dangerous thing', because if you remember an earlier example, namely,



the experimental evidence showed that

$$R \propto [\text{H}_2] \cdot [\text{NO}]^2$$

It is fair to say that it is this kind of complication that makes reaction rate study so important to chemistry. The reason for the discrepancy lies in the way the reaction proceeds. This particular example shows that the reaction does not proceed when collision occurs between two hydrogen molecules and two nitric oxide molecules. If it did, then doubling the concentration of the hydrogen molecules, $[\text{H}_2]$, would quadruple the rate of the reaction,

$$\text{i.e., } R \propto [\text{H}_2]^2$$

and doubling the concentration of the nitric oxide molecules would increase the rate of the reaction by a factor of four,

$$\text{i.e., } R \propto [\text{NO}]^2$$

The overall reaction rate would then be expressed

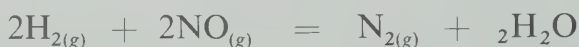
$$R \propto [\text{H}_2]^2 \cdot [\text{NO}]^2$$

which, from experimental evidence, is not the case.

How can this explained?

The way in which the reaction proceeds, called the '**reaction mechanism**', provides an answer.

The mechanism of the above reaction between hydrogen and nitric oxide is step-wise and the balanced equation



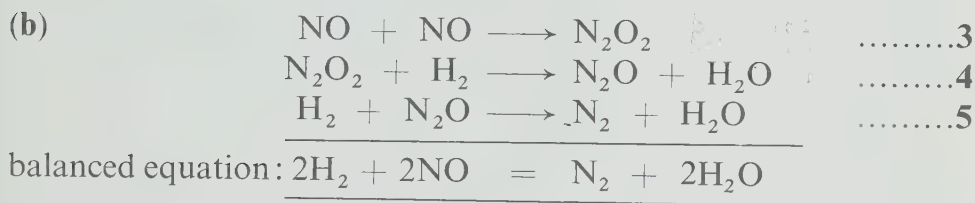
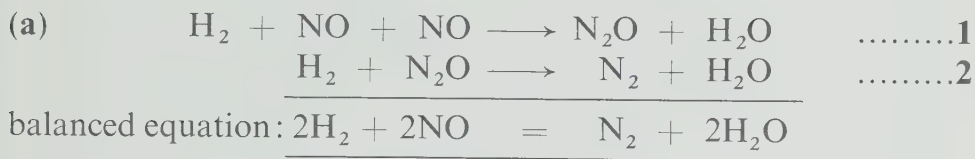
does not indicate the series of steps by which the reaction proceeds. But the experimentally determined rate equation

$$R \propto [\text{H}_2] \cdot [\text{NO}]^2$$

does. It suggests that a step must occur in this reaction which involves a ratio of one hydrogen molecule and two nitric oxide molecules, and that this step must be the overall rate determining step. This rate-determining step must be the slowest of the steps.

In the production line of a car manufacturer the overall production rate of the cars must be determined by the slowest step in the production line.

What are some of the possibilities of step-wise reactions involving hydrogen molecules and nitric oxide molecules? Two reaction mechanisms are suggested.



The first reaction mechanism, (a), is not acceptable, since if reaction 1 is to occur then two nitric oxide molecules and one hydrogen molecule must collide simultaneously. This means that, for reaction 1 to be effective, the simultaneous collision of three molecules is required. This type of collision is unlikely to occur.

Let us look at the exact meaning of the word *simultaneous*. Two molecules coming together, and then hit by a third molecule, is not a simultaneous collision. Three molecules colliding at exactly the same instant is a simultaneous collision. A simultaneous collision of three motor vehicles in motion is an extremely unlikely occurrence.

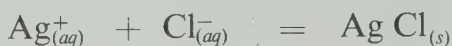
Using this reasoning, acceptable reaction mechanisms generally postulate steps involving two-particle collisions.

The more favourable reaction mechanism for the reaction between hydrogen and nitric oxide is described by equations 3, 4 and 5 above, that is, by a reaction mechanism involving bimolecular collisions in each step.

It is this kind of relationship, between the experimentally determined reaction rate and the theoretically interpreted reaction mechanism, which makes rate studies so important to chemistry. The study of reaction rates provides an insight into the mechanism of a reaction.

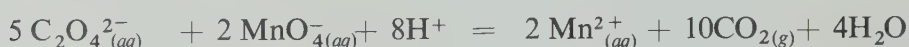
Reaction mechanism cannot be deduced from the balanced equation for the reaction.

Simple reactions involve few steps and we could predict that they will be fast. The equation



indicates a two ion collision resulting in precipitation of silver chloride. Provided that there are no complications with the water surrounding each of the ions, it would be possible to predict a fast reaction.

More complicated reactions involve many steps and are likely to be slow. Examples here are some redox reactions. Oxalate ions can be oxidized to carbon dioxide, CO_2 , by acidified oxidants, such as the permanganate ion or the dichromate ion,



This reaction is fairly slow at room temperature, but the similar looking reaction, oxidation of the iron II ion by the permanganate ion in an acid solution, is fast.



If the reaction mechanisms were known for the above reactions, then more accurate predictions could be made.

More Collision Theory — Energy Consideration

Consider the following mixtures of gases:

Mixture A — 1 mole of H_2 + 1 mole of O_2
in volume V litre at $T^\circ\text{C}$

Mixture B — 1 mole of H_2 + 1 mole of F_2
also in volume V litre at $T^\circ\text{C}$

Both mixtures have a number of similarities:

- both contain hydrogen;
- both contain molecules of similar size—oxygen and fluorine molecules are about the same size;
- the number of collisions occurring per second are the same in both. One hydrogen molecule in mixture A is likely to encounter 10^{12} oxygen molecules per second and one hydrogen

in mixture B is likely to encounter 10^{12} fluorine molecules per second.

How these figures are obtained is outside the scope of this book. You can find this information in an advanced physical chemistry text book.

Yet there is one major difference between the mixtures. Mix hydrogen and fluorine at room temperature, and you get an explosion; mix hydrogen and oxygen under the same conditions and no measurable reaction occurs! Why the difference? Does it mean that the collision theory is not a sound theory? Does it mean that all collisions are not effective collisions from a reaction point of view?

In one mole of a gas there are the Avogadro number of molecules, 6×10^{23} . If one molecule collides with other molecules 10^{12} times every second then the total number of collisions, in one mole of gas, every second is 10^{35} . Consequently, if collision were the only requirement for a reaction, reaction between gases would be over in a flash!

Since there are a very great number of collisions occurring, it follows that the velocity, and therefore the energy, of the molecules will vary considerably. When an individual molecule undergoes a collision, the magnitude of its velocity may be increased or decreased depending upon the direction of the collision. If the velocity of an individual molecule is increased then it becomes more energetic; if the velocity is decreased, the molecule becomes less energetic.

Temperature gives a measure of the average energy content of the molecules present. If the temperature is raised, then the average energy content of the molecules is increased. If the temperature is lowered then the average energy content of the molecules is decreased. Temperature increase has two effects:

- it increases the number of collisions
- it makes the collisions more violent

Temperature does not indicate the widespread (distribution) of energies that individual particles have. The following graphs indicate how an increase in temperature could change the distribution of molecular energies.

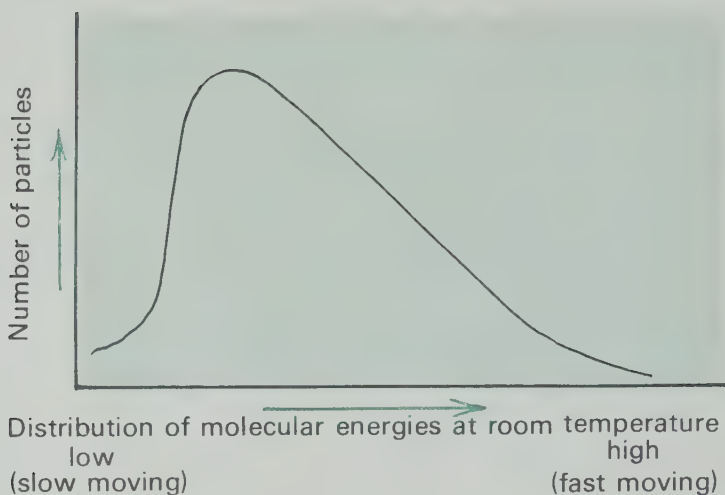


Figure 25. Distribution of molecular energies at room temperature

At a higher temperature the hump of the distribution curve moves to the higher energy end of the energy axis.

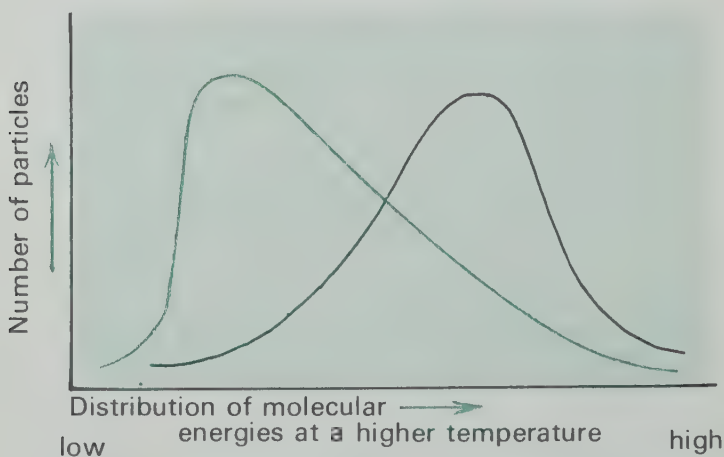


Figure 26. Distribution of molecular energies at a higher temperature

We have seen earlier how collisions occur with tremendous frequency (if tremendous is the right word to describe a frequency of the order 10^{35} times per second at room temperature), yet are ineffective, as in the case of hydrogen and oxygen. Raise the temperature and collisions becomes more effective. At a higher

temperature a mixture of hydrogen and oxygen explodes. Because the number of collisions is already extremely high it is reasonable to assume that the increase in energy content, rather than an increase in the number of collisions, makes temperature such an important rate-increasing factor. It is reasonable, then, to relate reaction rate to molecular energies. Because the energy of the particles is related to their movement it will be termed, initially, *kinetic energy*.

Consider two extreme examples of collision.

First, consider a gentle collision between two particles each having low kinetic energy. If the collision is gentle, then the electron clouds surrounding the molecules are not disturbed, and the repulsion between the electron clouds of each of the colliding molecules causes them to bounce apart again gently.

Second, consider a violent collision between two particles each having high kinetic energy, or a violent collision between a very high energy particle and particle of less energy. The collision may be sufficiently energetic for the electron clouds of the colliding species to be penetrated. Electron rearrangement results, giving a new species.

An obvious analogy presents itself. A collision between cars, one or both having high kinetic energy, results in considerable damage. While this damage is undesirable, damage from high energy molecular collision may be very desirable.

The reason why some substances react, even at very low temperatures (and the hydrogen-fluorine reaction is a good example), is because one or both species have more than just kinetic energy. They have a good chance of, or a good potential for, reacting. This potential for reaction is described as *potential energy*. Fluorine molecules, even at very low temperatures, have high potential energies.

Activation Energy

The energy required of a particle, or a combination of particles, before they have sufficient energy to react, is termed the **activation energy** and is denoted by the letters A.E.

Activation energy is the minimum energy (kinetic energy plus potential energy) species must possess before they will react.

Sometimes this energy is described as 'threshold' energy implying that this threshold, or barrier, has to be overcome before the reaction can proceed.

But it should not be assumed that every collision between molecules, or species, possessing the required minimum of energy results in the production of product(s).

Two things might happen:

1. The collision is effective, that is, bonds are broken, but an intermediate species forms and this then reacts with itself instead of with the desired reactant.

For example, high energy collisions between molecules of A and molecules of B may result in bond rupture to give a transitory atom of each. These atoms are just as likely to recombine with themselves as with the other species.

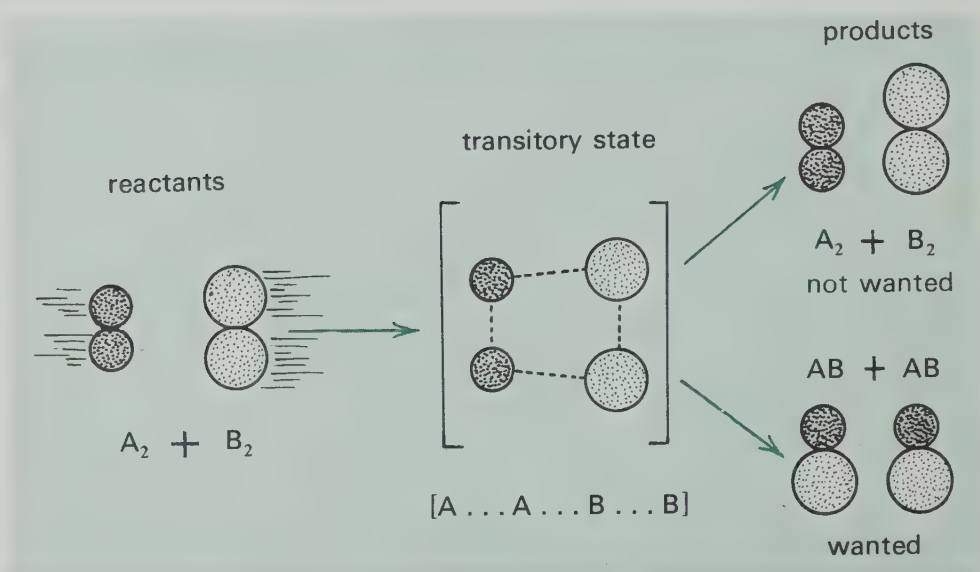


Figure 27

2. The collision *stereo-chemistry* is not favourable. The term stereo-chemistry refers to the orientation of each of the colliding species just prior to collision. If the positions adopted by each species just prior to collision are not favourable for the forming or breaking of the required bond, reaction may not proceed.

Suppose, in the hypothetical reaction between AB_2 and XY_2 ,

the mechanism demands A forming a bond with X. For this to happen during collision, A must hit or come close to X. The following orientation would be favourable for this to happen:

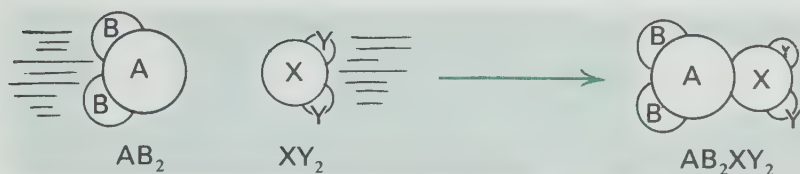


Figure 28

Whereas the orientation shown in figure 29 would not be favourable for an AX bond formation.



Figure 29

An analogy might be the best way of summing up the ideas so far presented in this topic.

Teams, of two, A and B, the reactants ($A + B$) set out to complete an obstacle course.

The first stage involves a steep climb up the side of the hill to a platform outside a narrow tunnel which passes through the hill. Only teams which are sufficiently energetic are able to reach the platform. Many start, some reach the platform, some are pushed or pulled up the hill by others and some simply fall back to the start. The tunnel through the hill is so narrow that a team of two, A and B, can pass through only if one of the team is carrying the other on his back. In chemical language this is the state of the activated complex—where both A and B are highly energetic and assisting each other in their passage through the tunnel. The team of A and B could now be given the symbol, AB^* . Many other teams of $A + B$ reach the tunnel entrance but are unable to pass through because one of the team is not carrying the other in the accepted way or orientation. Only those teams with the correct orientation are able to pass through the narrow tunnel. Once through the tunnel, the team of AB^* jump on to a



Figure 30

tandem bicycle which is provided and free-wheel to the finishing line. The bicycle is the bond holding the team together (A-B). If the finish is at a lower horizontal level than the start, then energy is released in the overall process; this is called an exothermic-type reaction path. If the finish is at a higher horizontal level than the start, then energy is absorbed in the overall process; this is called an endothermic-type reaction path.

These ideas are illustrated chemically by the following energy diagrams.

The difference in energy between A and B initially, and in their activated state, is the energy required to initiate the reaction. This energy is termed activation energy. Once in the activated complex state, energy is released as the products C and D form. In this example, the net release of energy is greater than intake, so the reaction is exothermic.

If the reaction is reversed, that is more energy is required to

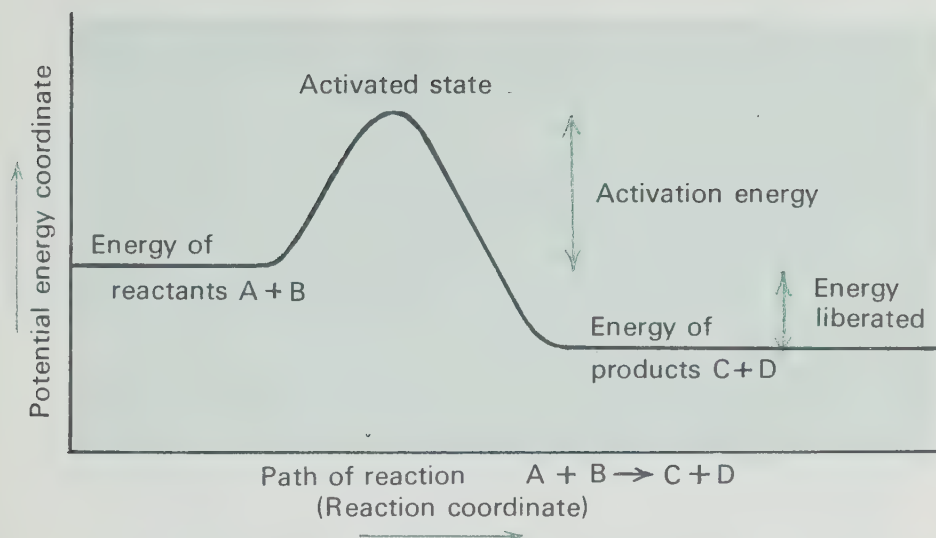


Figure 31. Energy diagram for an exothermic reaction

form the activated complex than is released—so the reaction is now endothermic.

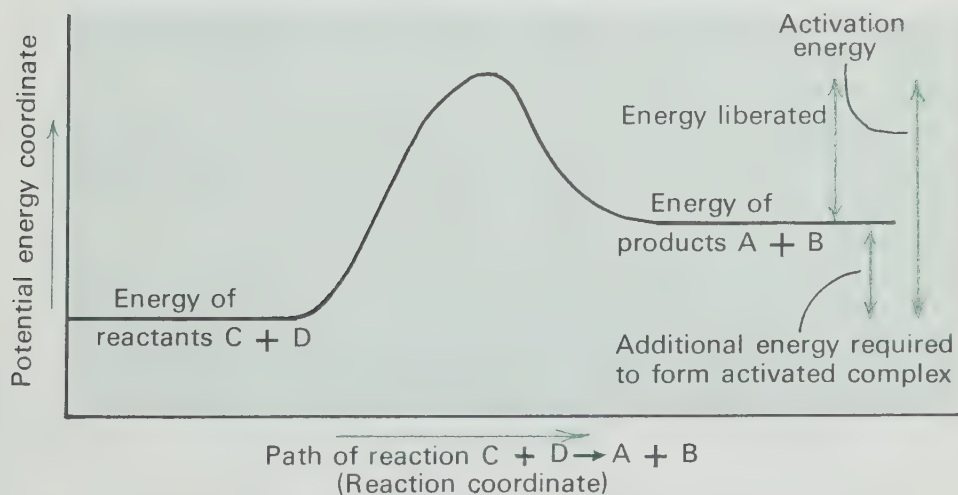


Figure 32. Energy diagram for an endothermic reaction

Catalysis can now be explained. Catalysts provide a reaction path requiring less activation energy if the catalyst is a positive one, and more activation energy if the catalyst is a negative one.

In positive catalysis the required activation energy can be achieved by more molecules, and hence the reaction goes faster.

The new reaction path is generally explained by the catalyst

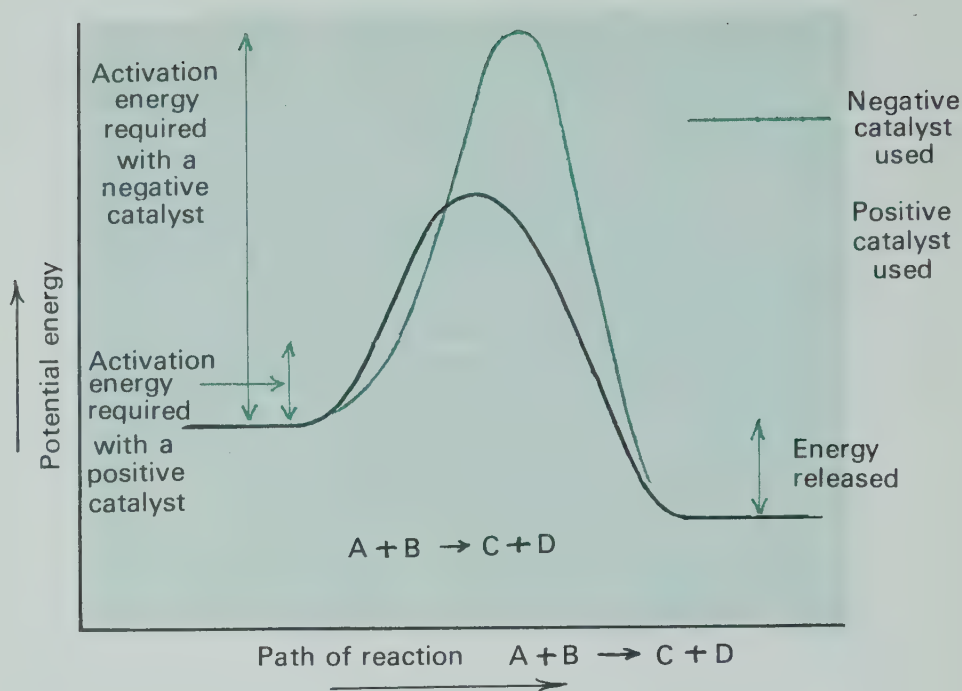


Figure 33. Influence of catalysts on required activation energies

forming a different activated complex requiring less activation energy.

The reduction of potassium chlorate (KClO_3) to potassium chloride (KCl), without using the positive catalyst manganese dioxide (MnO_2), follows the reaction path in which potassium perchlorate (KClO_4) is the activated complex.

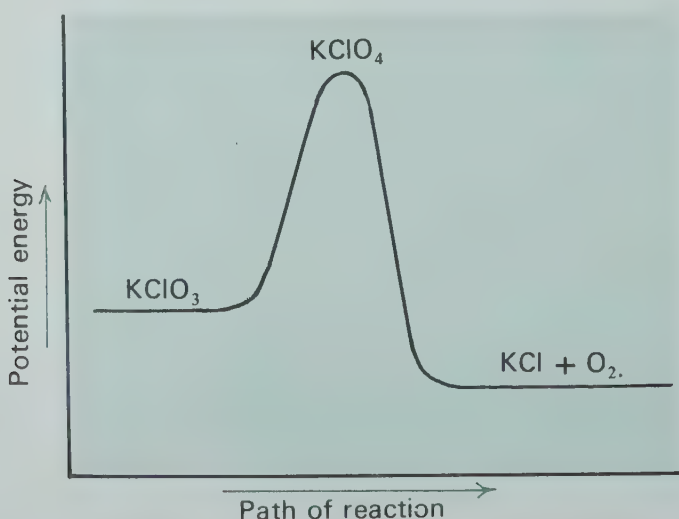
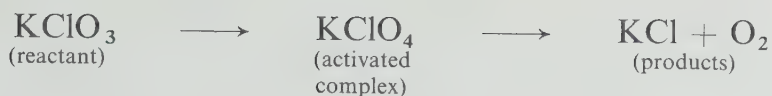


Figure 34. Energy diagram for the decomposition of KClO_3 without MnO_2



Using manganese dioxide (MnO_2) as the positive catalyst, the reduction of potassium chlorate to potassium chloride follows a different reaction path from that described above. Here the activated complex Mn_2O_7 requires less energy for its formation than does potassium perchlorate (KClO_4).

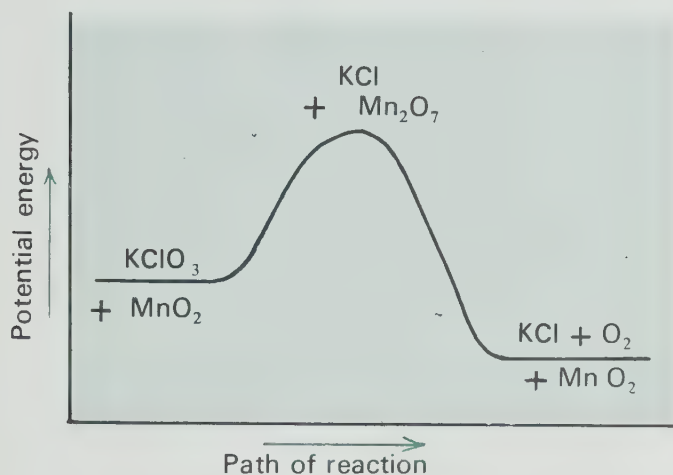
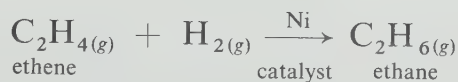


Figure 35. Energy diagram for the decomposition of KClO_3 with MnO_2

Many gaseous reactions use metallic catalysts to promote reaction rates. The adsorption theory is used to explain this type of catalysis.

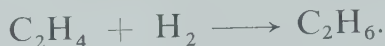
An example, from organic chemistry, is the hydrogenation of ethene.



The reaction occurs at the surface of the catalyst—hence the term adsorption. In most cases of surface adsorption on to metallic catalysts the result is a bond rupture, or a bond weakening, in one or more of the reactants. H_2 is adsorbed on to nickel as H atoms and the reaction



requires less activation energy than the reaction



As the H leaves the surface in the C_2H_6 the surface is again freed to continue catalytic activity.

In conclusion—does the collision theory successfully explain the four factors which affect reaction rates?

(1) The nature of the reactants

Because the energy of activation differs so widely from one reaction to another reaction, rates are going to vary just as widely.

(2) Concentration of reactants

Because concentration affects the number of collisions per unit time, the rate will change with concentration changes.

(3) The temperature

Because increase in temperature increases the average energy of the reactants and, on a smaller scale, increases the number of collisions per unit time, activation energy hurdles are more easily overcome. The reaction will proceed at a faster rate at a higher temperature.

(4) Catalysts

These form intermediate compounds or complexes which require lower activation energy than the original activated complex, and generally make the collisions more effective.

Summary

Although the principles governing the progress of chemical reactions seem almost self-evident, reaction rates and associated kinetics can present a rather complex picture to the young chemist—and to the not so young too, for that matter! But it is a fact that relatively simple principles underlie this study, and it is these principles rather than the associated detail and data that need to

be mastered. Of course, detail and data are needed to provide examples and illustrate the techniques, but should not be learnt in isolation from the principles being supported.

Although not conscious of it at the time, in earlier chemistry courses you probably made a rough-and-ready classification of reactions in terms of speed—fast and slow initially, with the addition of other groups between these extremes as your experience widened. This is hardly scientific; rate as a measure of concentration change in unit time provides a more scientific basis for accurate and precise observations.

For a given reaction, the laws of concentration and temperature dependence in determining rate, lead to a quantitative expression of rate—the rate equation; a logical follow-up to this is the classification of reactions according to this equation—the order of reaction classification.

Activation energy, within the reasonable framework of the collision theory, explains the observed dependence of rates on concentration, temperature and catalysts. Again it seems almost self-evident that active particles (those with excess energy) are the ones most likely to react. But it is these self-apparent ‘truths’, thought about and experimented on, that have given chemists a basis for the determination of reaction mechanisms and a glimpse into the processes which occur between chemical particles during reaction.

Reading List

Some helpful titles include the following publications, but this list is by no means exhaustive.

Abbott, D. and Andrews, R. *An Introduction to Chromatography*. Longmans, 1970.

Campbell, J. A. *Why do Chemical Reactions Occur?* Prentice Hall, 1965.

Harris, G. *Chemical Kinetics*. George Harrap, 1967.

Latham, J. L. *Elementary Reaction Kinetics*. Butterworth, 1962.

Nuffield Programme. *Catalysis*. (Chemistry Background Books) Penguin, 1969.

The Journal of Chemical Education, published monthly by the Division of Chemical Education of the American Chemical Society, has many articles and experiments on Reaction Rates during a year's issue. Refer to the index in the rear pages of the December issue.

Recent articles in this Journal include:

Ganesan, L. R. 'Kinetic Rate Equations' in *J.C.E.*, volume 46, page 226, 1969.

Swartz, Charles J. 'On Chemical Kinetics' in *J.C.E.*, volume 46, page 308, 1969.

Revision Questions

- 1 What factors can exert effects on the rates of chemical reactions? In each case explain how the effect is caused.
- 2 In reaction rate chemistry the term *order* is often confused with the term *molecularity*. Define each of these terms so as to show that no confusion exists as far as you are concerned.
- 3 The reaction of iodine with acetone $(\text{CH}_3)_2\text{CO}$, in the presence of an acid catalyst is found to be *first order* with respect to both acetone and hydrogen ions, but *zero order* with respect to iodine.
 - (i) What is meant by the term 'order of a reaction'?
 - (ii) Write an expression showing how the rate of the above reaction depends on the concentrations of the three species mentioned.

- (iii) Why is a study of the rates of chemical reactions of interest to chemists?
- (iv) Give a possible explanation as to why the iodine concentration does not affect the rate of this reaction.

4 The rate law for the reaction



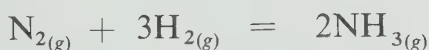
is given by

$$\text{rate} = k [\text{HI}]^2$$

- (i) How would the rate change if the concentration of the $\text{HI}_{(g)}$ was increased to twice its original value?
- (ii) How must the $\text{HI}_{(g)}$ concentration be changed in order to decrease the rate to one third its original value?
- (iii) What are the units of the rate constant k ?

5 Answer, true or false:

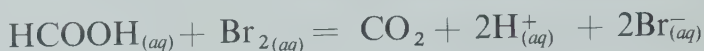
- (i) It is possible to change the rate of reaction by changing the temperature.
- (ii) Frequency of collision between reacting particles is increased by increased temperature.
- (iii) The rates of most reactions change as the reactions proceed even if the temperature is held constant.
- (iv) In a step-wise reaction the rate determining step is the slow one.
- (v) In the reaction



the ratio of the number of moles of ammonia formed to the number of moles of hydrogen used is 3 moles to 2 moles.

- (vi) If two molecules of reactant Y are present in the balanced stoichiometric equation representing a reaction involving Y, then this reaction is second order with respect to Y.
- (vii) An increase in temperature of 10 K always doubles the rate of any reaction.
- (viii) If a reaction is zero order with respect to any component then the rate of reaction is independent of the concentration of that component.
- (xi) A decrease in temperature lowers the rate of reaction for endothermic reactions.
- (x) A catalyst plays no part in a reaction it catalyses.

- 6 Chemical reactions vary greatly in their rates of reaction; some proceed at great speed, others proceed very slowly. Give examples of reactions at these extreme ends of rate. What are the reasons for these differences?
- 7 Consider the reaction between formic acid and bromine:



The initial concentration of Br_2 was measured and was found to be 0.01 M. After 2.5 minutes the Br_2 concentration is 0.0062 M.

Find the average rate of the reaction in terms of the consumption of bromine, and then in terms of the formation of Br^- ions.

How would you expect the rate of this reaction to change with:

- increased time,
 - a large bromine concentration at the start,
 - increased temperature,
 - a homogeneous catalyst,
 - diluting the reaction mixture by the addition of water?
- 8 The reaction paths for the reversible reaction



is shown by the graph energy plotted against reaction co-ordinate.

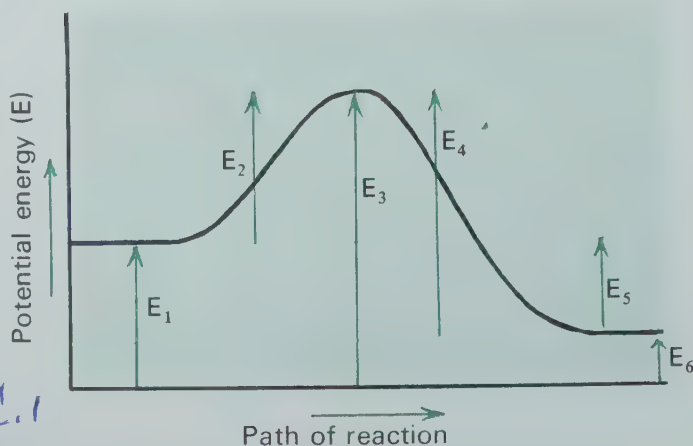


Figure 36

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- (i) Is the forward reaction exothermic or endothermic?
 - (ii) What value of E gives the energy of activation for the forward reaction?
 - (iii) What value(s) would be altered if a catalyst was used?
 - (iv) What value represents the heat of reaction for the reverse reaction?
- 9 Explain the following observations:
- (i) When hydrogen, $H_{2(g)}$, and oxygen, $O_{2(g)}$, are mixed at room temperature there is no reaction, yet when a platinum gauze is introduced an explosion results.
 - (ii) Sugar does not burn in air until strongly heated whereas the human body 'burns' sugar at 98.4°F (36.9°C).
 - (iii) Bottles of fine aluminium powder carry the warning 'DANGER—HIGHLY INFLAMMABLE' but aluminium saucepans are used for cooking.
 - (iv) A mixture of hydrogen, $H_{2(g)}$, and chlorine, $Cl_{2(g)}$, in a clear container can be exploded by exposing to sunlight.
- 10 What are the essential features of a catalyst? What general explanations can you give for catalytic activity?

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AUTHOR

Stanley, R.J.

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Rates of Chemical Reactions

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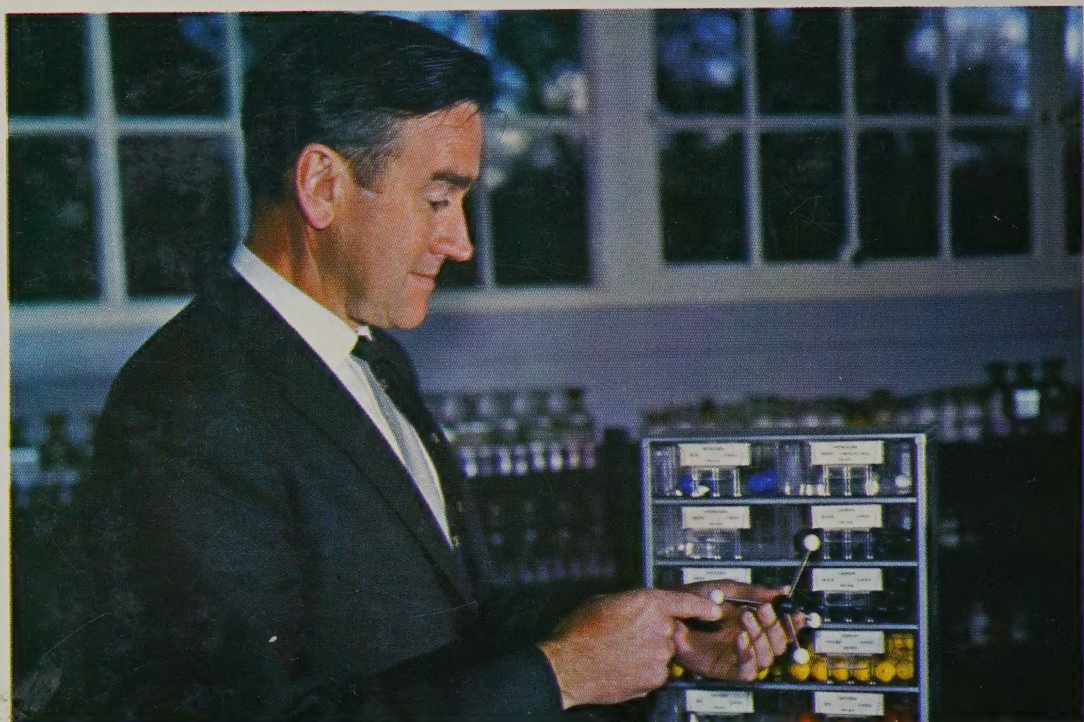
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Holding a Bachelor of Science degree from the University of Adelaide, he also has a diploma of education, is a member of the Australian College of Education and an associate of the Royal Australian Chemical Institute.

Mr Stanley holds the rank of Lieutenant Colonel in the C.M.F., where his work earned him an Efficiency Decoration, and an O.B.E. in 1968. In his spare time he enjoys painting and flying light aircraft. From 1950-1959, Mr Stanley taught at Scotch College, Adelaide, then was at St Peter's College from 1960-69. In 1969 and 1970, he taught at Marlborough College in England, and had the opportunity of seeing at first hand some of the new developments in school science in England.

Besides his work for and in school chemistry, he has been President of the South Australian Science Teachers' Association, and chief examiner for Leaving Chemistry for the Public Examinations Board in South Australia.